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THE ELEMENTS

OF

THERMAL CHEMISTRY.

THE ELEMENTS

OF

THERMAL CHEMISTRY

BY

M. M. PATTISON MUIR, M.A., F.R.S.E.,
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ASSISTED BY

DAVID MUIR WILSON.

> "We rely on the truth for aid against ourselves." EMERSON.

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X

PREFACE.

It is universally acknowledged that a chemical operation presents two aspects to the investigator; it involves a change in the form or distribution of matter, and a change in the form or distribution of energy. The greater number of the chemical text-books pay very little heed to the latter of these changes. Indeed it is only within recent years that any serious attempt has been made to measure the changes of energy which accompany chemical changes of matter. Such measurements, so far as they have yet gone, have been almost wholly confined to determinations of the quantities of heat which enter or leave a chemical system during its passage from one definite state to another. Any exact applications which can at present be made of the laws of energy to chemical processes must then, for the most part, be based on the results of thermo-chemical investigation.

This book is intended to present a connected account of the methods and results of the most important researches which have been made in Thermal Chemistry. It does not in any way pretend to be an exhaustive treatise on the subject; its object is to deal with principles, and methods of investigation,

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rather than with details. The book is adapted for the use of students who have a fair knowledge of the principles of chemistry, and who are also conversant with the outlines of the study of energy. A sketch of the preliminary study required is given in the earlier paragraphs of the first chapter.

I have endeavoured to deal with the various parts of the subject from the point of view of the chemical, rather than from that of the physical, inquirer. The two-sidedness of all the problems examined in Thermal Chemistry makes this a subject in which one is very ready to go astray.

The original intention was to produce a condensed and somewhat modified translation of Prof. Alexander Naumann's *Lehr- und Handbuch der Thermochemie;* but as the work proceeded this intention was abandoned. The general scope and conception of Naumann's book were thought to be unsuited to the wants of the English student. Some parts of the subject which are dealt with by Naumann in great detail appeared to me to be too strictly physical to warrant their introduction into a book on thermal chemistry; other parts should rather, I think, find a place in a book on pure chemistry. On the other hand there are many subjects of great importance which have received especial attention since the publication of Naumann's treatise; among these may be mentioned the recent work of Thomsen on the classification of acids and bases, and on the relative affinities of acids.

I have also regarded the whole subject from a point of view essentially different from that occupied by Prof. Naumann. I have endeavoured to gain a general conception of the subject as a whole, and to indicate the mutual relations of its parts; I have also striven to place the facts before the student as far as possible independently of theories, and then to gather up these facts and consider them in the light of theory. For this reason I have said very little regarding what some would look on as fundamental principles of the subject—the law of maximum work, and the interpretation of thermo-chemical data in terms of the molecular theory—until the last chapter of the book.

The book is divided into two parts. The first part is devoted to the statement and consideration of the various branches of thermal chemistry: the second comprises most of the well-established data on which the science is built; these data are classified and tabulated in five appendices, which it is hoped will prove of considerable service to students. Data relating to melting and boiling points are omitted, because their insertion would have made the book very bulky, and also because they are to be found fully and carefully collected in Dr Carnelley's tables. No data are given relating to specific heats of solids or of solutions; for these the student is referred to Naumann's work, and to Clarke's *Constants of Nature.*

Where the thermal value of the same operation has been measured by various experimenters, preference is always given to the results obtained by Thomsen; for this reason many numbers which are found in Naumann's work are omitted from the appendices.

Chemical formulæ are used sometimes as synonymous with the names of the bodies formulated, and sometimes with a definite quantitative meaning: I think the context will always indicate where a quantitative meaning is to be given to these formulæ.

The principal calorimetric methods adopted by Thomsen, Berthelot, and other experimenters, are described, and the more important instruments are figured. References are given to all original papers or treatises of importance.

I have made free use not only of Naumann's *Thermochemie,* but also—and to a very large extent—of Thomsen's *Thermochemische Untersuchunjen,* and Berthelot's *Essai de Chimique Mécanique.*

I have been much assisted in preparing this book by Mr Wilson, whose name appears on the title-page; and also by Mr D. J. Carnegie, B.A., Scholar of Gonville and Caius College, who has kindly read the whole of the proofs and made many useful suggestions.

M. M. PATTISON MUIR.

CAMBRIDGE, *December* 1885.

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TITLES OF JOURNALS CONTAINING MEMOIRS TO WHICH REFERENCES ARE MADE.

ABBREVIATED TITLES.	FULL TITLES.
Phil. Trans.	*Philosophical Transactions.*
Proc. R. S.	*Proceedings of the Royal Society.*
C. S. Journal.	*Journal of the Chemical Society.* [Memoirs and Proceedings, 3 vols. (1841–1847). Journal, **series 1**, 15 vols. (1848–1862). ,, **series 2**, 15 vols. (1863–1877). ,, **Transactions** and **Abstracts** paged separately, from 1878 to present time. The volumes of this Journal are sometimes referred to by numbers beginning with volume 1 of series 1, and running on consecutively to the present time.]
Phil. Mag.	*Philosophical Magazine.* [**Series 1 to 5.**]
Chem. News.	*The Chemical News.* [Beginning from 1860.]
Nature.	*Nature.* [1879, and onwards.]
Brit. Ass. Reports.	*Reports of the British Association for the Advancement of Science.* [1831, and onwards.]
Proc. R. I.	*Proceedings of the Royal Institution of Great Britain.* [1851, and onwards.]
Amer. Journ. of Sci. and Arts *Sill. Amer. Journal.*	*American Journal of Science and Arts;* since 1880 the title is *American Journal of Science.* [Conducted by Sillimann, and subsequently by Sillimann and Dana. **Series 1 to 3.**]
Pogg. Ann.	*Poggendorff's Annalen der Physik und Chemie.* [1824–1876.]
Wied. Ann.	*Wiedemann's Annalen der Physik und Chemie.* [Continuation of *Pogg. Ann.* from 1877; frequently quoted in memoirs, &c., as *Ann. Phys. Chem.* **Series 2.**]
Annalen.	*Liebig's Annalen der Chemie und Pharmacie.* [Continued since Liebig's death under same title.]
J. für prakt. Chemie.	*Journal für praktische Chemie.* [**Series 1 and 2.**]
Ber.	*Berichte der Deutschen Chemischen Gesellschaft.* [Abstracts of papers published elsewhere are paged consecutively with the transactions until 1883; from 1884 and onwards the abstracts, **Referate**, are paged separately.]
Zeitschr. für Krystallog.	*Zeitschrift für Krystallographie und Mineralogie.* [1877, onwards.]
Sitzber. der Wiss. Akad. zu Berlin.	*Sitzungsberichte der Akademie der Wissenschaften zu Berlin.* [1854, and onwards.]

ABBREVIATED TITLES.	FULL TITLES.
Compt. rend.	*Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.* **[1835, onwards.]**
Mém. de l'Acad.	*Mémoires de l'Académie Royale des Sciences de l'Institut de France.* **[1816, onwards.]**
Ann. Chim. Phys.	*Annales de Chimie et de Physique.* **[Series 1 to 6.]**
Bull. Soc. Chim.	*Bulletin de la Société Chimique de Paris.* **[1864, onwards.]**
Ann. Min.	*Annales des Mines.* **[Series 1 to 6.]**

CORRECTIONS AND ADDITIONS.

PAGE

58. *Add note* to this effect: 'The value of the heat of formation of H_2SO_4 may be more shortly calculated as follows, when the data $[S, O^3, Aq] = 142, 417$ are obtained (see p. 57): a solution in water of SO_3 contains H_2SO_4, therefore

$$[S, O^3, Aq] = [S, O^3, H^2O, Aq] = 142, 417;$$

but

$$[H^2, O] = 68{,}360; \therefore [H^2, O, S, O^3, Aq] = 142, 417 + 68{,}360 = 210{,}777.$$

Now

$$[H^2SO^4, Aq] = 17{,}850; \therefore [H^2, S, O^4] = 210{,}777 - 17{,}850 = 192, 927.\text{'}$$

70. Eighth line from top: *for* '$[C, H_4]$' *read* '$[C, H^4]$'.

88. Seventeenth line from bottom: *dele* 'organic'.

125. Second line from bottom: *after* 'compound' *add* 'at that pressure'.

143. Sixth line from bottom: *after* 'density' *add* 'of many gaseous compounds'.

1. ~~158.~~ Plate facing this page; at bottom of plate: *for* 'Temp. – 18°' *read* 'Temp. = 18°'.

179. *Note* 1: *for* 'Proc. R. S.' *read* 'Proc. R. I.'

195. Eleventh line from top: *for* 'transferred' *read* 'transformed'.

207. Second line from bottom: *for* '$[H, Cl, O^3Aq]$' *read* '$[H, Cl, O^3, Aq]$'.

235. Sixth line from bottom: *for* 'C^{13}' *read* 'O^{13}'.

256. Third line from top: *for* '$H_3P_2O_7$' *read* '$H_4P_2O_7$'.

288. Fourth column of figures, top line of column: *for* '05' *read* '0·5'.

THERMAL CHEMISTRY.

CHAPTER I.

PRELIMINARY SKETCH OF THE SUBJECT.

THERMAL Chemistry treats of the mutual relations between chemical and thermal phenomena. The study of this branch of natural science can be profitably undertaken only when some knowledge has been gained of the general laws of heat and chemistry.

A brief outline of the more important parts of the preliminary thermal and chemical study required for properly grasping the teaching of thermal chemistry is all that can be given in this book. The student must fill in the outline for himself.

SECTION I. *Chemical change. The conservation of mass.*

1. Chemistry is that branch of physical science which concerns itself with the more marked and far-reaching changes in the properties of matter which occur in nature or can be produced in the laboratory.

When water is exposed in an open vessel to a temperature lower than 0° C. it is changed into solid ice. When the temperature of ice is raised above 0° C. the ice is changed into liquid water. When an electric current is passed through water, it is changed into two colourless gases, each characterised by properties which sharply distinguish it from the other, and neither shewing much resemblance to the water from which both have been obtained. If these gases are mixed and an electric spark is passed through the mixture, the gases completely disappear and water is produced.

The change of water into ice, and the reverse change of ice into water, may be taken as a representative physical change.

The change of water into a mixture of gaseous oxygen and hydrogen may be taken as a representative chemical change.

2. *The mass of matter which takes part in any change whether physical or chemical remains unaltered.*

This statement which is the outcome of many centuries of inquiry is known as the principle of the conservation of mass, or the principle of the indestructibility of matter. On this principle the science of chemistry is based.

3. From the chemical point of view matter may be divided into two classes, elements and compounds. A weighed quantity of very finely divided iron is strongly heated; the iron glows for a few minutes, and when the glowing has ceased there remains a quantity of rust the mass of which is greater than that of the iron at the beginning of the experiment. A weighed quantity of potassium chlorate is strongly heated; it melts, and a gas is produced in which a burning body burns much more brilliantly and rapidly than in ordinary air. When gas ceases to be evolved a white solid remains the mass of which is less than that of the potassium chlorate used.

Iron is a typical element; potassium chlorate is a typical compound.

An element may be defined as a kind of matter which can undergo chemical change only by combining with some other kind, or kinds, of matter; the mass of the product of such a change is therefore always greater than the mass of the element.

A compound may be defined as a kind of matter which can undergo chemical change either by combining with some other kind of matter, or by itself separating into two or more other kinds of matter, the mass of each of which is therefore smaller than that of the compound.

4. By the composition of a compound is meant a statement of the elements which can be obtained from it, and of the quantities of those elements which can be obtained from a specified quantity of the compound.

The composition of every chemical compound is fixed and unalterable. Thus 100 parts by weight of pure water always contain 88·88 parts by weight of the element oxygen, and 11·12 parts by weight of the element hydrogen; or we may say the elements are combined in the ratio of 8 to 1. Hydrogen and oxygen form two compounds; in the first (water) the ratio in which the masses of oxygen and hydrogen are combined is 8 : 1; in the second (hydrogen peroxide) the ratio is 16 : 1. Nitrogen and oxygen form five compounds in which the masses of oxygen and nitrogen are combined in the following ratios (1) 1 : 1·75; (2) 2 : 1·75; (3) 3 : 1·75; (4) 4 : 1·75; (5) 5 : 1·75. These cases are representative of chemical compounds in general. To every element a number may be given which expresses the smallest mass of that element which combines with unit mass of some element chosen as a standard. These numbers also express the smallest masses of the various elements which severally combine with each other.

The standard element is hydrogen; the unit mass is 1 gram, or 1 grain, or 1 lb.

Thus the following numbers represent the *combining weights* of various elements; oxygen = 8, chlorine = 35·5, sodium = 23, calcium = 20. These numbers tell us that 8 or a simple multiple of 8 parts by weight of oxygen, 35·5 or a simple multiple of 35·5 parts by weight of chlorine, 23 or a simple multiple of 23 parts by weight of sodium, and 20 or a simple multiple of 20 parts by weight of calcium, severally combine with 1 part by weight of hydrogen to produce definite chemical compounds. Further these numbers tell us that 8 or a simple multiple of 8 parts by weight of oxygen combine with 20 or a simple multiple of 20 parts by weight of calcium, that 23 of sodium combine with 35·5 of chlorine &c., to produce definite chemical compounds.

The symbol of an element, e.g. H, O, Cl, or of a compound, e.g. H_2O, HCl, represents a definite mass of that element or compound, and when the element or compound is gaseous, the symbol also represents a definite volume of the body[1].

---

[1] The student is supposed to be familiar with the use of chemical symbols before proceeding further. (See also *post*, pars. 30—36).

5. In considering chemical phenomena it will be convenient to use such expressions as 'a changing system,' 'the system undergoing chemical change,' and the like.

Thus in the case already referred to of the electrolysis of water, the quantity of water through which the current passed was the changing system. If the water had been brought into contact with a piece of the metal sodium, one of the gases obtained by electrolysis, viz. hydrogen, would have been produced, and a new body, composed of sodium, hydrogen, and oxygen, (sodium hydroxide), would have been formed and dissolved in a portion of the water. In this case the system undergoing chemical change would have consisted of water, sodium, hydrogen, and sodium hydroxide. When a candle burns in air the changing system is composed of candle, air, and the products of the burning of the candle.

SECTION II. *Changes of energy. The conservation of energy.*

6. Every chemical operation consists of two parts, a change in the form of the matter comprising the system, and a change in the form of the energy of the system.

Energy is the power of doing work; work being defined as 'the act of producing a change of configuration in a system in opposition to a force which resists that change.'[1]

7. Any material system may be considered as made up of several particles each of which is so small that, for the purposes of the special investigation undertaken, the distances between the parts of these particles (if they have parts) may be neglected. These particles at any moment must be arranged in some definite way relatively to each other; this 'assemblage of relative positions is called the configuration of the system.'[2]

When mutual action and reaction occurs between two systems so that there is a change in the configurations of the systems, one system is said to exert force on the other.

Force then is a name given to a two-sided transaction when that transaction is looked at from the standpoint of one of the transactors. The change of configuration produced in one of the mutually acting systems necessitates change in the motions of the parts of that system, in other words necessitates an acceleration of these parts. The force exerted by one system on the other may be measured by the product of the mass of matter moved and the acceleration produced in that mass. Or, in other words, as mass into velocity = momentum, the force may be measured by the change of momentum which it produces per unit of time. When the mutual actions between the two systems are completed let us suppose that the first system has lost, and the second has gained momentum; then the first system has also lost energy or power of doing work, and the second system has gained an exactly equal quantity of energy.

---

[1] Clerk Maxwell, *Matter and Motion*, art. 72.

[2] Id. *loc. cit.* art. 4.

8. It is customary to speak of a force as acting on a body or system, but it should not be forgotten that force is merely a convenient name, the use of which helps us to study the mutual actions of bodies, and systems of bodies, which study is the real business of physical science. Nevertheless in dynamics the actions of forces are measured and compared without constant reference to the acting and reacting bodies; and the conception implied in the word force has been so much used apart from the conception of two, or more, mutually acting bodies, that the name has almost ceased to be a mere name, and is frequently used as if it represented a real thing.

Remembering that behind the word force there is always a reality, we may speak of the application of a force, or even of the work done by a force.

9. Suppose a man lifts a weight through a space of 3 feet, and places it on a support at that distance from the ground; we have here two mutually acting systems, (*a*) the man, and (*b*) the weight and the earth. System (*a*) does work against the resistance of system (*b*); and when the work is done, system (*b*) has gained just as much energy as system (*a*) has lost. For, let the weight be now attached to the machinery of a clock, and let the support be removed; the weight slowly descends to the ground, and in doing so it communicates energy to the clock, which energy is spent in overcoming the friction of the various parts, the resistance of the air to the motion of the pendulum &c. Had the weight not been raised from the ground it would have been of no use as a source of energy to the clock. The whole

system, clock and raised weight, therefore possesses energy because of the configuration of its parts; and when the configuration is changed in a certain way this energy is lost to the system.

In this example it is clear that the man has done work against the resistance of the weight. But we may say that the man has exerted force, and, abstracting the notion of the man, we may say that work has been done by a force on the weight.

10. In order to measure this force we must know the mass of the weight raised, the time occupied in the movement of the weight from its point of rest on the ground to its point of rest on the support, and the space through which the weight has been moved.

Suppose the velocity of the movement to have been uniform throughout the whole time. Then putting $v =$ velocity, $s =$ space, and $t =$ time, we have

$$v = \frac{s}{t}.$$

Then, as force is measured by mass moved into velocity, and as the velocity was uniform, we have

$$F = mv;$$

where $F =$ force, and $m =$ the mass of the weight moved.

Now let us suppose that the weight was in motion when the force began to act upon it; further let the initial velocity be v, let the force continue to act for a very short time t, and let the velocity at the end of this time be v'. Then the momentum of the weight at the beginning of the time t was mv, and at the close of the time t the momentum was mv'. And, since a force is measured by the change of momentum it produces when acting for unit time, it follows that[1]

$$Ft = m(v' - v).$$

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[1] We can now define the unit of force as that force which acting on unit mass for unit time produces unit acceleration in the mass. The most commonly used unit of force is called the *dyne*, and is defined to be that force which acting for one second on a mass of one gram, produces in it a velocity of one centimetre per second. The unit of work is the *erg*, which is defined to be the work done by one dyne when acting through a distance of one centimetre.

The student ought carefully to study some treatise on the measurement of forces &c., e.g. Clerk Maxwell's *Matter and Motion*, chaps. I. II. and III.; or the same author's *Theory of Heat*, chap. IV.

From this equation we can find the space through which the weight has been moved by the application of the force F acting for the time t. The time t is very small, therefore we may take the average velocity during this time as the arithmetical mean of the velocities at the beginning and end of the time, that is, as

$$\tfrac{1}{2}(v + v').$$

But as space described is equal to velocity into time, it follows that

$$s = \tfrac{1}{2}(v + v')\,t.$$

Then multiplying together the two equations we get

$$Fts = \tfrac{1}{2}m\,(v'^2 - v^2)\,t\,;$$

and dividing by t, we have

$$Fs = \tfrac{1}{2}mv'^2 - \tfrac{1}{2}mv^2.$$

11. Now Fs measures the work done by the force acting on the body whose mass is m, while that body moves through the space s, in the same direction as that in which the force is applied. But when work is done on a body that body gains energy. In the case before us this gain of energy is attended with an increase of the velocity of the body, and the energy gained is measured by half the product of the mass into the difference between the squares of the final and initial velocities. This form of energy which is connected with the motion of a body, or system of bodies, is called *kinetic energy*, and is to be distinguished from *potential energy*, which is the energy connected with the configuration of the parts of a body or system of bodies.

If the force F acted on the body with mass m in a direction opposite to the motion, then the force would act as a resistance to be overcome by the moving body. In this case the kinetic energy of the body would be decreased until the body came to rest, when the whole work done by it would be equal to the whole kinetic energy which it possessed when the force began to act[1].

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[1] If the time during which the force acts is not so short that the mean velocity may be considered as equal to the arithmetical mean of the velocities at

12. The energy of a system of mutually acting and reacting bodies will be composed of two parts, (1) the potential energy, that is the energy due to the relative positions of the bodies which form the system; and (2) the kinetic energy, that is the energy due to the motions of these bodies. Besides this, if the system as a whole is in motion it will possess a certain amount of kinetic energy due to this motion. In such a system there will sometimes be constant change of configuration and of the motions of the parts; there will therefore be constant change of potential into kinetic energy and *vice versa*. If we know the motions of the parts at any moment we can calculate the kinetic energy by the method already given, viz. by multiplying the mass of each part by half the square of its velocity and taking the sum of these products. But we have no generally applicable method for calculating the potential energy. The relation between configuration and potential energy appears to vary for almost every system. The theory of potential energy is much more complicated than that of kinetic energy. In a theoretical system of bodies such as is treated of in abstract dynamics the only conditions present are the configuration and the motions of the parts of the system. Hence the energy which is not due to motion must be due to configuration. But although we know that part of the energy of actual material systems is sometimes dependent on configuration, e.g. the energy of a coiled watch spring, yet we are not able to state the exact relation between the energy and the configuration of such systems.

13. If one system does work on another, the amount of energy lost by the first system is exactly equal to the amount of energy gained by the second; if therefore both systems are included in one larger system, the total energy of this larger system is unchanged. Similarly, if a part of one system does work on another part of the same system, the total energy of

the beginning and end of the action, then "by dividing the whole time of action of the force into small parts, and proving that in each of these the work done by the force is equal to the increase of kinetic energy of the body, we may, by adding the different portions of the work and the different increments of energy, arrive at the result that the total work done by the force is equal to the total increase of kinetic energy" (Clerk Maxwell). See for more details Clerk Maxwell's *Theory of Heat*, pp. 87—92 (6th Ed.).

the system is unchanged, although one part of it has lost and another part has gained energy. This is the principle of the conservation of energy. This principle is thus stated by Clerk Maxwell[1].

"*The total energy of any material system is a quantity which*
"*can neither be increased nor diminished by any action between*
"*the parts of the system, though it may be transformed into any*
"*of the forms of which energy is susceptible.*"

This principle has been proved to be absolutely true for systems fulfilling certain conditions, and it has been experimentally verified in cases where the energy of the systems examined takes the form of heat, electrification, magnetisation &c., indeed it is "the one generalised statement which is found to be consistent with fact, not in one physical science only, but in all."[2]

14. If the configuration of a system is changed by the action of an external agent, then the energy of the system either increases or diminishes during this change. If the energy increases the agent has done work in the direction of the change of configuration; if the energy decreases the system has done work on the external agent, and hence the force exerted by the external agent is in the direction opposite to that of the change of configuration. Hence "a complete knowledge of the mode in which the potential energy of a system varies with the configuration would enable us to predict every possible motion of the system under the action of given external forces, provided we were able to overcome the purely mathematical difficulties of the calculation."[3]

15. In examining the action of forces on material systems, it is of course necessary to specify the directions in which these forces are applied. Thus force may be exerted by an external agent on a system with the production of a displacement of the system from one configuration to another, or force may be

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[1] *Matter and Motion*, art. 74. The whole of chap. v. of this little book should be carefully studied.

[2] Id. *loc. cit.* art. 73. See also Id. *Theory of Heat*, pp. 92—3. (6th Ed.), also Tait's *Heat*, pp. 17—20.

[3] Clerk Maxwell, *Matter and Motion*, art. 83.

exerted by the system against an external agent which resists the displacement of the system.

When we come to deal with the changes of energy which accompany the action of the so-called chemical forces, we shall find that one of the main difficulties is to specify the direction in which the forces are applied.

16. The energy of actual material systems depends on the states of these systems at any moment. The state of a system is conditioned by the values of such variables as chemical composition, pressure, temperature, electrical potential &c. Hence the changes in the energy of a system will depend on the changes in the values of these, and other variables.

Now in physical science we wish to measure changes of energy, and to connect these with changes in the values of the chemical composition, the electrical potential &c. of the system. To do this we must start with the system in some definite and defined state, we must bring it into another definite state, and we must measure the change of energy which accompanies this passage from the one state to the other[1].

The loss or gain of energy is independent of whether the passage from one state to another is effected directly, or through a series of intermediate states.

In thermal chemistry we especially endeavour to measure energy-changes by thermal methods, and to connect these with changes of chemical composition.

SECTION III. *Heat. First and second laws of thermodynamics.*

17. Heat is not a material substance, because the quantity of it can be indefinitely increased, and it can also be destroyed.

Heat is a form of energy, because heat is produced by the application of mechanical work, and work is done by the action of heat.

18. Moreover, *there is a definite quantitative relation between the amount of work done and the quantity of heat produced or destroyed*[2].

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[1] The reader should study arts. 86 to 91 in *Matter and Motion.*

[2] For a clear account of the progress of the doctrine that heat is a form of energy see Tait's *Heat*, chap. IV. pars. 21 to 31.

This application of the principle of the conservation of energy to thermal phenomena is usually known as the first law of thermodynamics.

Joule, and others, have measured the mechanical equivalent of heat.

Joule found that in order to raise the temperature of one pound of pure water from 60° to 61° F. an amount of work must be done which is measured by 772·55 foot-pounds at sea-level in the latitude of Greenwich. If this is translated into metrical units, the statement runs thus: in order to raise the temperature of one kilogram of water from 0° to 1° C. an amount of work must be done which is measured by 423·99 kilogram-metres. This number, 772·55 foot-pounds or 423·99 kilogram-metres, is usually called Joule's equivalent.

19. In all natural occurrences there is a transformation of energy from one form to another; e.g. energy of electrical separation may be transformed into heat, energy of chemical separation may be transformed into light or heat, or into electrical energy, and so forth. All forms of energy can be directly or indirectly transformed into heat.

20. It is necessary to distinguish between higher and lower forms of energy, in other words it is necessary to distinguish between energy which is more available and energy which is less available for doing mechanical work.

So far as heat is concerned, the only way in which this form of energy can be used for doing mechanical work is by letting it down from a body at a higher to a body at a lower temperature. A certain quantity of heat, therefore, as it exists in a hot body is more available than the same quantity of heat as it exists in a colder body.

21. *If all the heat in any body, or system of bodies, is at the same temperature, then no mechanical work can be obtained from that body, or system, except by bringing it into contact with another body at a lower temperature.*

This is one of the many forms in which the second law of thermodynamics may be stated[1].

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[1] Compare Maxwell, *Theory of Heat*, p. 153 (6th Ed.) with Tait, *Heat*, p. 60.

If the system under consideration is regarded as comprising the whole physical universe, and if the temperature of this system is supposed to have become uniform, then no work can be obtained from this system by any method known to us, although the system may contain large stores of energy in the form of heat.

22. The running down of energy from a higher, i.e. a more available, to a lower, i.e. a less available form, is known as the dissipation, or perhaps better, the *degradation of energy*. Now as in every operation occurring in nature there is a transformation of energy, and as any transformation of energy, so far as we know, involves a running down of a portion of the energy transformed, the total energy of the material universe is continually becoming less and less available, it is continually undergoing degradation[1].

If this is so, it becomes a question of the greatest importance to determine what portion of a given quantity of energy in a stated form can be changed into work. So far as heat-energy is concerned this question has been answered by Carnot, who proved that the fraction of the total quantity of heat which is converted into mechanical work by a reversible heat-engine depends entirely on the difference between the temperatures of the source of heat and the refrigerator. Carnot also proved that a reversible heat-engine is a perfect engine, that is to say, that no other engine can convert so large a fraction of the total heat into mechanical work[2].

SECTION IV. *Application of thermal methods to chemical problems.*

23. Every chemical reaction, as we have seen, is composed of two parts; a transformation of matter, and a transformation of energy.

In applying thermal methods of measuring energy-changes to the investigation of chemical phenomena, we start with a definite chemical system in a definite state, we allow this system to pass into another definite state and we measure the quantity of heat produced during this chemical change.

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[1] Compare Tait's *Heat*, pars. 78—79.

[2] See Clerk Maxwell's *Theory of Heat*, chap. VIII., or Tait's *Heat*, chap. IV. par. 81 *et seq.*

24. If we assume that the whole of the energy which has been lost by the system in the passage from the initial to the final state has appeared in the form of heat, then the measurement of this quantity gives us a measurement of the difference between the energies of the system in the two states. In many cases, however, a portion of the energy of the original system is directly changed into some form other than heat, e.g. into electrical energy, sound-energy, or radiant energy. If the amount of energy thus transformed is measured, or if the experimental conditions are arranged so that the electrical or other energy is finally changed into heat and the total quantity of heat is measured, then the total loss of energy suffered by the chemical system, in its passage from the defined initial state to the specified final state, is determined.

25. The difficulties of thermal chemistry really begin when we try to use the results of such measurements as are indicated in the preceding paragraph. The problem is to measure the quantity of energy which has entered or left a given system during a definite chemical change. But the chemical change is always accompanied by and intermingled with physical changes, and it is usually very difficult, if not indeed impossible, to disentangle the two parts, the chemical and physical parts, of the complete change. Moreover it is scarcely possible at present correctly to interpret the meaning of the phenomena presented by the chemical change.

SECTION V. *Hypothesis regarding the mechanism of chemical changes.*

26. That matter has a grained structure, in other words, that a mass of matter is not homogeneous, is proved by (1) the phenomena presented by the passage of a ray of white light through a refractive medium, (2) the phenomena of contact electricity, (3) the phenomena of liquid films e.g. soap-bubble-films, and (4) the behaviour of gases.

These four groups of phenomena cannot be explained in terms of any hypothesis which asserts that an apparently homogeneous mass of matter is really homogeneous; the phenomena force us to accept the hypothesis that were any piece of matter, e.g. a drop of water sufficiently magnified, we should see that it is built up of a vast number of small particles, each of which possesses the properties that distinguish water from all other kinds of matter. The hypothesis further asserts that these small parts of any material body act and react in accordance with the principle of the conservation of energy. When the body is heated the motion of agitation of these small particles is increased. These particles are called molecules.

27. Confining our attention to gases we may adopt the following definition:

'A gaseous molecule is that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas.'[1]

28. The pressure of a gas on the walls of a containing vessel is, on this hypothesis, an effect of the impact of the molecules, and this again depends upon the number and the velocity per unit of time of these molecules. If the number of molecules in a given volume is increased, i.e. if the density of the gas is increased, the pressure is proportionately increased. This is the law of Boyle.

Assuming that the temperature of a gas represents the mean kinetic energy of the molecules of that gas, then if two gases are in thermal equilibrium,

$$MV^2 = M_1V_1^2;$$

where M and M_1 represent the masses, and V_1^2 and V^2 the mean squares of the velocities of the molecules of the two gases. But if the pressures of the two gases are equal,

then $$MNV^2 = M_1N_1V_1^2;$$

where N and N_1 represent the number of molecules in unit volume of the two gases.

29. From these two equations it follows that

$$N = N_1;$$

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[1] Clerk Maxwell, article 'Atom' in *Encycl. Britannica* (9th ed.).

that is, *when two gases are at the same pressure and temperature the number of molecules in unit volume of either gas is the same.*

And as the density of a gas is equal to the product of the mass of the individual molecules into the number of molecules in unit volume, and as the number of molecules in unit volume of the two gases is the same, it follows that *the densities of two gases at the same temperature and pressure are proportional to the masses of their individual molecules.*

The two statements in italics have been long known in chemistry as Avogadro's law; they are now, however, raised from the rank of empirical statements to that of dynamical deductions from the fundamental hypothesis of the molecular theory of matter[1].

These statements are of the utmost importance in chemistry, as they furnish a means of determining the relative weights of the molecules of all gaseous bodies.

30. The statements may be put more shortly in this form:

Equal volumes of gases, at the same temperature and pressure, contain equal numbers of molecules.

Consider the following chemical changes; the temperature and pressure remaining constant.

(1) Hydrogen + Bromine (gases) = Hydrobromic acid (gas);
volumes 1 + 1 = 2.

(2) Hydrogen + Chlorine (gases) = Hydrochloric acid (gas);
volumes 1 + 1 = 2.

Now, if equal volumes of gases contain equal numbers of molecules, there must be as many molecules of bromine gas as of hydrogen taking part in change (1), and as many molecules of chlorine as of hydrogen taking part in change (2). Let there be p molecules of hydrogen, then there are p molecules of bromine and p molecules of chlorine in the combining volumes of these gases. But $2p$ molecules of hydrobromic acid gas, and $2p$ molecules of hydrochloric acid gas, are produced. But each molecule of hydrobromic acid is composed of hydrogen and bromine, and each molecule of hydrochloric acid is composed of hydrogen and chlorine. Hence, each molecule of hydrogen, and each of bromine (or each molecule of hydrogen, and each of chlorine) has separated into at least two parts, and each of these parts, or half-molecules, of hydrogen has combined with a half-molecule of bromine (or chlorine) to produce a molecule of hydrobromic (or hydrochloric) acid gas.

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[1] The student should carefully peruse chap. XXII. of the *Theory of Heat.*

31. Hence we conclude that, although the molecules of hydrogen move about as wholes when hydrogen is heated, nevertheless these molecules are themselves composed of parts, and these do part company when hydrogen and bromine, or hydrogen and chlorine, mutually react to produce hydrobromic or hydrochloric acid gas.

By extending this method of inquiry to a great many chemical changes in which hydrogen takes part, we arrive at the conclusion that any molecule of hydrogen is composed of two parts, and that during at least many chemical reactions a separation of the molecule into its parts occurs.

32. The parts of the molecule of an elementary gas are called atoms.

The molecule of hydrogen is composed of two atoms; it is a diatomic molecule. And as hydrogen is the standard substance in terms of which the relative weights of the molecules, and atoms, of other gases are stated, we say that the atomic weight of hydrogen is one, and that the weight of the molecule of hydrogen, represented by the symbol H_2, is two.

33. To determine *approximately*[1] the relative weight of the molecule of any gas it is only necessary to determine the density of that gas referred to hydrogen, and to multiply this number by two. Thus oxygen is sixteen times heavier than hydrogen, hence the molecular weight of oxygen gas is thirty-two.

The following table gives the mean results obtained in determining the densities of the thirteen elementary bodies which have been gasified up to the present time.

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[1] See *post*, par. 34.

Molecular weights of elementary gases.

Name of element.	Temp. of observation (approximate).	Density H = 1.	Molecular weight.
Hydrogen	0°	1	2
Nitrogen	0°	14·02	28·02
Oxygen	0°—1400°	15·96	31·92
,, ozone		23·93	47·88
Sulphur	500°	95·55	191·88
,,	800°—1400°	32·2	63·96
Chlorine	200°—1200°	35·36	70·74
Cadmium	1000°	56·8	112·1
Phosphorus	500°—1000°	62	123·84
Arsenic	600°—800°	150·5	299·6
Bromine	100°	78·75	159·5
,,	about 1500°	58·9	?
Selenion	850°	110·7	236·4
,,	1400°	80·5	157·6
Mercury	400°—1000°	99·85	199·8
Iodine	200°—800°	125·85	253·07
,,	1300°—1500°	68·7	[?126·52]
Tellurium	1400°	127	250

34. It will be noticed that the numbers in column IV. are not always exactly double those in column III. The value obtained for the density of a gas is necessarily subject to errors of experiment; nor in chemical investigations do we attempt to determine these values by any very refined experimental methods. We rather find, with the greatest care and refinement of experiment possible, the value to be assigned to the combining weight of each element, i.e. the mass of the element which combines with one part by weight of hydrogen or with 7·98 parts by weight of oxygen[1]. The molecular weight of an element must be equal to, or a multiple of its combining weight, and the molecular weight of a compound must be equal to the sum, or to a multiple of the sum of the combining weights of its constituent elements. Hence it follows, that accurate determinations of the combining weights of different elements, and approximately accurate determinations of the densities of these elements and their compounds in the state of gases, furnish the data required

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[1] See *ante*, par. 4.

for finding the most probable values to be assigned to the molecular weights of the elementary and compound gases in question.

Thus, the combining weight of chlorine has been very carefully determined by Stas to be 35·37. An experiment which may be easily and rapidly performed shews that chlorine is approximately $35\frac{1}{2}$ times heavier than hydrogen; hence the molecular weight of chlorine gas is evidently very nearly equal to $35·37 \times 2 = 70·74$.

Again the combining weight of beryllium, as very accurately determined by Nilson and Pettersson, has been found to be 4·54. The chloride of this metal contains beryllium and chlorine united in the proportion of 4·54 to 35·37, hence the molecular weight of this chloride is $n\ (35·37 + 4·54)$. Beryllium chloride has been recently gasified by Nilson and Pettersson; the density of this gas is about $40\frac{1}{2}$ times that of hydrogen, therefore the molecular weight of the gas is about 81. Now $35·37 + 4·54 = 39·91$; hence the molecular weight of the gas is $39·91 \times 2 = 79·82$.

35. In paragraph 32 it was said that the parts of the molecules of an elementary gas are called atoms. The atoms of the elements are the ultimate portions of matter with which we have to deal in chemistry.

Now the molecule of a compound gas must be built up of two or more elementary atoms (refer back to the reactions studied in par. 30). It is evident that no molecule of a compound can contain less than one atom of each element present in the compound.

36. Hence we arrive at the following definition of the maximum value to be given to the atomic weight of an element:—

The maximum atomic weight of an element is the smallest mass, in terms of hydrogen as unity, of that element in a molecule of any compound thereof.

The word *maximum* is introduced into this definition because the value assigned to an atomic weight by this method may be too large, but is certainly not too small. For, consider what the definition implies. It implies that a number of gaseous compounds of the element whose atomic weight is required are known, that these have been carefully analysed, and the density of each has been determined. It implies that the mass of the given element in each of these compounds is stated in parts per molecule. Then the smallest mass is said to be the maximum atomic weight of the element. But it is possible that a new gaseous compound of this element may be prepared which shall contain, per molecule, a smaller mass of the element than is found in a molecule of any of its compounds at present known. In this case the value now assigned to the atomic weight will be decreased.

Take the following data for determining the atomic weight of oxygen :—

Data for determining the atomic weight of oxygen.

Gaseous compound.	Density H = 1.	Molecular weight (approximate).	Analysis, stated in parts per molecule.
Carbon dioxide	22·07	44·15	31·92 oxygen + 11·97 carbon
Sulphur dioxide	32·4	64·9	31·92 „ + 31·98 sulphur
Sulphur trioxide	43·4	86·9	47·88 „ + 31·98 „

Were no other gaseous compounds of oxygen known than those in this table, we should adopt the number 31·92 as the maximum value to be given to the atomic weight of this element. But consider the following numbers :—

Gaseous compound.	Density H = 1.	Molecular weight (approximate).	Analysis, stated in parts per molecule.
Carbon monoxide	13·9	27·96	15·96 oxygen + 11·97 carbon
Water	8·9	17·99	15·96 „ + 2 hydrogen
Nitric oxide	15	30·00	15·96 „ + 14·01 nitrogen

Hence the value previously given is too large, and the maximum atomic weight of oxygen must now be taken as 15·96.

The greater the number of gaseous compounds of a given element which have been examined, the greater is the probability that the maximum value assigned to the atomic weight is the true value.

37. The quotient $\frac{\text{molecular weight of element}}{\text{atomic weight of element}}$ is called the *atomicity*[1] of the elementary molecule. As it is sometimes said that for the majority of the elements $\frac{\text{molecular weight}}{\text{atomic weight}} = 2$, it may be well to place before the student the actual data which we have concerning the value of the quotient in question.

Atomicity of elementary molecules. (Only thirteen elements have been gasified.)

Monatomic.	Diatomic.	Triatomic.	Tetratomic.	Hexatomic.
Cadmium	Hydrogen	Oxygen as ozone	Phosphorus	Sulphur (450° to about 550°)
Mercury	Chlorine		Arsenic	
Iodine (at about 1500°) [? Bromine at about 1800°]	Bromine Iodine (200° to about 1000°) Oxygen Sulphur (at 800° and upwards) Selenion (at 1200° and upwards) Tellurium Nitrogen	Selenion (700°–800°)		

38. There are other methods than that based on the application of Avogadro's law for determining the values to be assigned to the atomic weights of the elements. The most generally applicable of these methods is that founded on the law of Dulong and Petit.

This generalisation states that the product of the specific heat of any solid element into the atomic weight of that element is a constant number, the mean value of which is 6·4.

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[1] The term atomicity has been used as synonymous with maximum valency of an elementary atom; but chemists are now fairly well agreed to employ the term with the meaning given to it in the text.

If this is granted it follows that $\frac{6{\cdot}4}{\text{specific heat of solid element}}$ = atomic weight of the element (approximately).

But the specific heat of a solid body is a number which varies with the temperature and with the physical state of the body. Thus, the specific heat of diamond at moderate temperatures is different from that of graphite, and the specific heat of any variety of carbon has a much larger value at high than at low temperatures.

Several elements have not as yet been obtained in the solid form, or not obtained in sufficient quantity and purity to enable satisfactory determinations of their specific heats to be made.

39. Another method by the use of which the values of some atomic weights have been fixed is based on the law of isomorphism, which states, that identity of crystalline form is conditioned only by the number and arrangement of the atoms in the molecules of the isomorphous (*i.e.* crystallographically identical) compounds. Hence, on this hypothesis, if the number of atoms in the molecule of one compound is known, the number of atoms in the molecule of another compound which crystallises in the same form is known also; and hence, if the atomic weights of all the elements except one in the second compound are known, the atomic weight of the remaining element can be determined. Thus the value assigned to the atomic weight of chromium by the use of the methods founded on Avogadro's law, and on the law of Dulong and Petit, is 52·4; from this, and from the results of analysis, the molecular weight and composition of the green oxide of chromium are represented by the formula $n\,Cr_2O_3$, where $Cr = 52{\cdot}4$ and n is a whole number[1]. But ferric oxide and chromic oxide are isomorphous, hence ferric oxide is probably represented by the formula $n\,Fe_2O_3$. If this is so then $Fe = 56$; because 104·8 parts by weight of chromium are combined with 48 of oxygen in chromic oxide, and 112 of iron are combined with 48 of oxygen in ferric oxide; in other words, 104·8 parts by weight of chromium in the oxide are replaced by 112 of iron without change of crystalline form. But 104·8 represents the weight of two atoms of chromium, therefore, as identity of crystalline form is associated

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[1] As this oxide has not been gasified we cannot decide what is the value of n.

with identity of numbers of atoms, 112 represents the weight of two atoms of iron, and therefore the atomic weight of iron is 56.

The application of the method of isomorphism to determine atomic weights is however beset with many difficulties. Sometimes a group of atoms is crystallographically equivalent to a single atom; sometimes it is very difficult to determine the exact meaning to be given to the expression 'isomorphous compounds.' In a word, our knowledge of the connections between crystalline form and chemical composition is too small to enable us to assent to the law of isomorphism in the form in which it is usually stated.

40. Besides these three physical methods, there are various chemical methods for finding values for the atomic weights of elements. These may be broadly grouped together as methods based on analogies of composition and reactions between compounds, the molecular weight of one or more of which is already known.

Thus, compounds of hydrogen with (1) sulphur, (2) selenion, (3) tellurium, are known. These compounds shew very close resemblances in their chemical behaviour, hence probably their composition is very similar. The composition of the molecule of the sulphur compound is represented by the formula SH_2; hence the composition of the other compounds will probably be represented by the formulæ SeH_2 and TeH_2 respectively. These formulæ are quite in keeping with the analyses of the compounds, provided the value 78·8 is given to the atomic weight of selenion and 125 to that of tellurium.

But there is no generally applicable chemical method for finding either molecular or atomic weights. Each case has to be discussed more or less as a separate question[1].

Concluding remarks to Chapter I.

41. The student must bear in mind that the molecular theory of the structure of matter is a theory, not a statement of facts, but that it is a theory which has very much aided the advance of physical science. He should also particularly

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[1] The subject of atomic and molecular weights is of the utmost importance; it has been treated in detail and fully illustrated by examples in "A Treatise on the Principles of Chemistry" by the author.

remember that the theory has been worked out in any detail only for gases: indeed it may be said that for gases alone have we any kinetic theory.

We shall use this theory as our chief guide in attempting to interpret chemical phenomena which occur among gaseous or gasifiable bodies, when we are chiefly paying attention to these phenomena from the point of view of the composition of the changing chemical system. For it should be remembered that any chemical occurrence presents two distinct although closely connected aspects. It presents us with a transformation of matter, and a transformation of energy. In treatises on general chemistry, the former transformations, or we may almost say the initial and final stages of the former transformations, are alone studied. In treatises on heat, attention is particularly directed to the second class of transformations. In thermal chemistry, an attempt is made to combine both aspects of the occurrences which we call chemical changes, and to generalise the relations between the two kinds of transformations.

42. A chemical change, if it is possible to isolate the chemical part from accompanying physical parts of a process, will be regarded as essentially a change in the distributions, configurations, and motions of atoms which together form a molecule or molecules. Strictly speaking this definition can be applied only to gases, and even then it is difficult if not impossible to keep within the terms of the definition. Nevertheless it is well that we should have such a definition. The energy-changes which we shall have to study will be regarded as changes accompanying alterations in the distributions, configurations, and motions of atoms. But here again we shall find ourselves compelled to relax the definition, and frequently to leave the inquiries as to the exact mechanism whereby the transformations of energy we are dealing with are brought about, more or less unanswered.

43. The physical inquirer regards the properties of any kind of matter as conditioned by the nature of the molecules, by the number and arrangement of these molecules in a given volume, and by the motions of these molecules. The molecule may have parts; if so the total kinetic energy of the material system must be composed of two parts, one part due to the

motion of agitation of the molecules as wholes, and the other due to the rotational motions of the parts of the molecules. The properties about which the chemist seeks to gain knowledge are rather regarded as chiefly conditioned by the nature, number, arrangement, and motions of the parts of the molecules which build up the body he examines. To gain such knowledge he must study the action of various external agents, e.g. heat, other chemical bodies &c. on the substance whose properties he investigates. He is thus bound to study changes; he does not so much desire to know the properties of this body or that system considered apart from other bodies or systems, as to learn how the properties of mutually acting systems are modified by those actions, and more especially when he studies thermal chemistry he wishes to learn something of the connections which exist between the changes in the nature, number, distribution, and motions of atoms, on the one hand, and the changes of energy on the other hand.

44. It is proposed to divide the subject matter of thermal chemistry into the following groups.

I. Statement and illustrations of methods of inquiry.
II. Applications of thermal methods to chemical questions.
III. Applications of the same methods to questions which are partly chemical and partly physical.
IV. Discussion of the chemical interpretation to be given to thermal data, in the light of the prevalent theories regarding matter and energy.

CHAPTER II.

METHODS OF INQUIRY USED IN THERMAL CHEMISTRY.

SECTION I. *Measurement of heat or Calorimetry.*

45. As heat is a form of energy it may be measured by transforming it into mechanical work and measuring the work done in terms of some unit e.g. the erg. But heat may also be measured by causing it to produce some definite physical change in a given mass of a given substance. 'When two equal portions of the same substance in the same state are acted on by heat in the same way so as to produce the same effect, then the quantities of heat are equal'[1].

46. The standard substances usually employed are (1) ice, and (2) water.

If ice is employed, the unit of heat is defined to be that quantity of heat which will change unit mass of ice into the same mass of water without any rise of temperature, the pressure being 760 mm. throughout the change.

If water is employed, the unit of heat is defined to be that quantity of heat which will raise the temperature of unit mass of water at some standard temperature through one degree.

As unit mass, one pound, or one grain, or one kilogram, or one gram, may be used.

In almost all thermochemical researches the unit mass actually employed has been one kilogram or one gram. If the former, the unit of heat is generally called a large calorie or a kilogram-unit; if the latter, the unit of heat is called a small calorie or a gram-unit. If the heat is measured by allowing it to melt ice without raising temperature, then the unit of heat is called the ice-calorie; if the heat is measured by causing it to raise the temperature of water through one degree, then the unit of heat is called the water-calorie. One ice-calorie is equal to 80·025 water-calories.

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[1] Maxwell, *Theory of Heat*, p. 54 (6th ed.).

47. The quantity of heat required to raise the temperature of unit mass of water through one degree depends upon the initial temperature of the water. This initial temperature must therefore be stated. Berthelot[1] employs water at 0° C; Thomsen[2], water at 18—20° C. The difference in the value of the calorie dependent on this difference of initial temperature does not exceed one in a thousand.

The unit of heat generally adopted in this book is defined to be that quantity of heat which is required to raise the temperature of one gram of pure water at 18—20° C through one degree centigrade[3].

48. Various forms of calorimeters are used in thermochemical investigations. The instrument usually employed for measuring the quantities of heat produced in reactions between substances in aqueous solutions consists of a platinum vessel, capable of containing from 500 to 1000 c.c., placed inside another vessel of silver or thin sheet iron, with water between the two vessels. The liquids which react on each other are brought to the same temperature, and are then mixed in the platinum vessel, and the rise of temperature in the contents of this vessel is registered. The outer vessel serves to prevent any loss of heat to the surrounding air. Many devices are adopted for securing this end (see par. 49). Berthelot surrounds his calorimeter proper with several other vessels of silver and sheet iron, each furnished with a cover, a thermometer, and a stirrer. Thomsen prefers to employ fewer exterior vessels; he works in a room the temperature of which does not vary more than 0°·1 to 0°·2 C during the time his experiments proceed.

[1] *Mecanique Chimique fondée sur la Thermochemie*, **1.** XXXI.

[2] *Thermochemische Untersuchungen*, **1.** 23.

[3] Some data are quoted from Berthelot or his pupils; these are given in Berthelot's calories which are referred to water at 0°.

The specific heat of the liquids which are mixed in the calorimeter must be carefully determined throughout a considerable range of temperature.

Special kinds of calorimeters have to be employed for special purposes. When the heat produced during the burning of an element or compound in oxygen, or in another gas, is to be measured, a bulb of platinum is usually employed. This is placed in a vessel, or vessels, containing a known mass of water at a known temperature. The combustion proceeds in the bulb, and the heat produced is employed in raising the temperature of the water in the calorimeter. If the products of the combustion are gaseous they must be collected in a specially constructed apparatus and their weight determined. Sometimes small quantities of material must be employed e.g. in the action of nitric acid upon benzene. Sometimes the reaction must proceed in a closed vessel e.g. when one of the reacting substances is changed by contact with air. Sometimes the reaction must be conducted at a temperature considerably higher than the ordinary; in such a case the apparatus is enclosed in an outer case, the space between the two parts of the apparatus is filled with air or with some liquid, and the temperature is maintained at the required degree by immersing the whole apparatus in a bath.

The most delicate thermometers must of course be employed; each instrument must be carefully calibrated and the errors of zero point &c. determined from time to time.

When a reaction occurs between two liquids it is very necessary to keep the liquids constantly agitated; the water in the outer part of the calorimeter must also be maintained in constant agitation. Various forms of agitators have been devised by Berthelot, Thomsen, and others. Thomsen employs a small electromagnetic engine to work the agitator of his apparatus.

49. In this paragraph short descriptions are given of the principal calorimeters commonly used by Berthelot and Thomsen. For details regarding these instruments, and for descriptions of the various precautions taken, and the corrections which must be made, the student is referred to the memoirs and books to which references are

given below[1]. He should more especially consult the pages of Berthelot's *Mecanique Chimique* and Thomsen's *Thermochemische Untersuchungen.*

A. Calorimeters for measuring the thermal values of reactions between aqueous solutions, or between a solid and water, or a gas and water; e.g. the neutralisation of acids by alkalis in aqueous solutions, or the action of water on copper sulphate, or the action of hydrochloric acid on water.

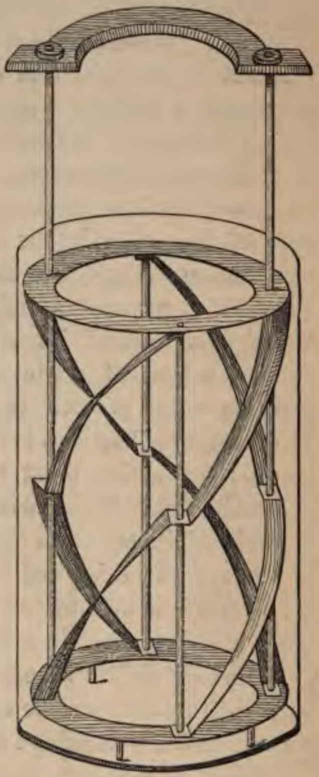

FIG. 1.

The temperature of the liquids to be mixed must be the same when the reaction begins; all the heat evolved in the process must be used in raising the temperature of the mixed liquids.

[2]Berthelot employs a fairly large platinum vessel (about 600 c.c. capacity); if the liquids act upon platinum he uses flasks made of very hard Bohemian glass. As stirrer he employs thin sheets of platinum or glass arranged in a screw-like fashion (see fig. 1). The stirrer is moved backwards and forwards in the liquid through an arc of 30° to 35°. Berthelot places his calorimeter proper

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[1] *References to memoirs &c. where calorimeters and calorimetric methods are described.*

BERTHELOT. *Essai de Mecanique Chimique.* **1.** *Book* 2; Méthodes expérimentales; also *loc. cit.* supplement.

THOMSEN. *Thermochemische Untersuchungen.* **1.** pp. 18—24; 27—35; **2.** 8—18; 45—47; 68—70; 305—8; 339—353; **3.** 222—225.

FAVRE and SILBERMANN. *Ann. Chim. Phys.* (3) **34.** 359; **36.** 44.

FAVRE. *Compt. rend.* **66.** 788; **73.** 717.

BUNSEN. *Pogg. Ann.* **141.** 1. See also in connection with the use of Bunsen's ice-calorimeter, SCHULLER and WARTHA, *Ber.* **8.** 1011; and **10.** 1298. NILSON and PETTERSSON, *Ber.* **11.** 385. DONATH, *Ber.* **12.** 744. v. THAU. *Wied. Ann.* **13.** 85.

[2] *Mecanique Chimique.* **1.** 110.

(*A* fig. 2), with its cover and thermometer (*A′* fig. 2), in an outer vessel of thin copper, which is immediately surrounded by another vessel of silver with a cover (*B* fig. 2); this vessel is placed in a considerably larger double walled vessel of sheet iron (*C* fig. 2), containing from 10 to 14 litres of water between the walls, and furnished with a stirrer (*D* fig. 2) and thermometer (*E* fig. 2). The whole series of vessels is surrounded with thick felt. The calorimeter proper rests upon three pieces of cork, the silver vessel likewise rests upon cork. The water is placed in the outer vessel some days before an experiment is to be made. The whole apparatus stands on a wooden bench in a large room protected from the sun's rays. All the liquids, the thermometers, the stirrers, &c., are placed in this room some days before the experiments begin so that every thing may be as nearly as possible at the same temperature.

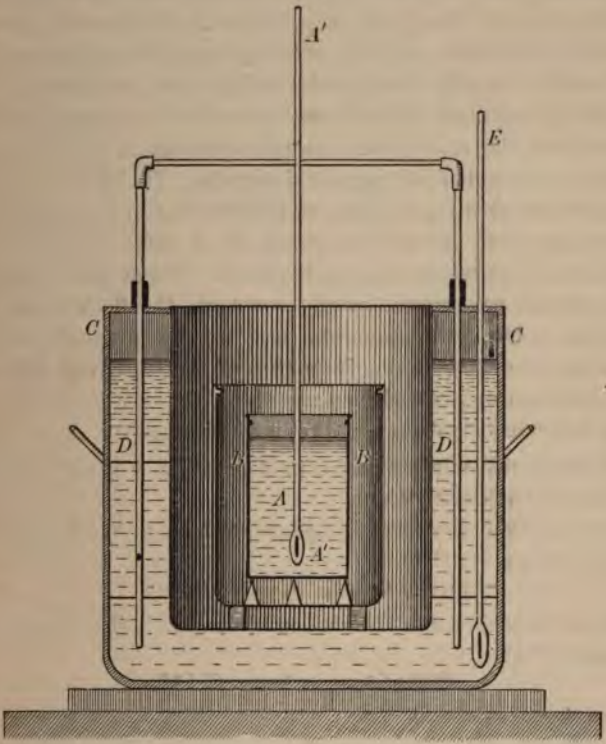

FIG. 2.

The liquids to be mixed, e.g. aqueous solutions of sulphuric acid and caustic soda, are placed in flasks made of thin hard glass with very short necks, (if long-necked flasks are used the difference between the temperature of the liquid in the flask and that in the neck may amount to one or two-tenths of a degree C.); the flasks are placed on straw rings inside silver vessels until the contents attain a constant temperature.

Let us suppose it is desired to determine the thermal value of the reaction between equivalent quantities of sulphuric acid and potassium sulphate, each in dilute aqueous solution. Two large flasks, containing about 4 litres each, are filled with the carefully prepared solutions; after these, and the other parts of the apparatus, have been for some days in the experimenting room, two flasks, holding 300 c.c. each, are filled with the respective liquids, one of the liquids is poured into the calorimeter, the stirrer is set in motion and the temperature is noted at regular intervals. The flask containing 300 c.c. of the other liquid is set on a straw ring in a metallic vessel, the contents are stirred by means of a thermometer and the temperature is noted at regular intervals. When the temperature of each liquid has become nearly constant, the flask is seized by a wooden holder, the contents are rapidly emptied into the calorimeter, (the stirrer being in motion all the time) and the course of the thermometer is noted for some time.

The following numbers are taken at haphazard[1].

First liquid (sulphuric acid, 49·0 grams in 4 litres) 300 c.c. in calorimeter; temp. = 23°·45.

Second liquid (potassium sulphate, 87·1 grams in 4 litres) 300 c.c. in a flask; temp. = 23°·44.

Mixed liquids; temp. = 23°·33.

Hence, mean temp. before mixture = 23°·445; temp. after mixture = 23°·33.

Fall of temperature = 0°·115.

Experiment repeated.

Temp. of first liquid = 23°·43; of second liquid = 23°·405.

Mean temp. = 23°·4175.

Temp. of mixed liquids = 23°·305.

Fall of temperature = 0°·1125.

The thermometers used indicated a difference of 0°·005.

If one of the liquids which mutually react is very volatile (e.g.

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[1] For a statement and discussion of the necessary precautions and corrections, see Berthelot, *loc. cit.* **1.** 171—180.

hydrocyanic acid or cyanogen chloride), or changes on exposure to air (e.g. concentrated sulphuric acid, phosphorus chloride &c.), or gives off vapours (e.g. concentrated acid solutions), then it must be weighed in a small tube or bulb of thin glass. This bulb is placed on a small platinum support, immersed in the liquid in the calorimeter (which is stirred till the temperature is constant), and then broken by a little crusher of platinum or glass. If the reaction is rapid and is attended with evolution of much heat, e.g. the mutual action of water and phosphorus trichloride, the small bulb has a long fine-drawn out neck, the end of which is broken in the calorimeter so that the liquid slowly passes into the bulb. In some cases the bulb is furnished with a tube bent twice at right angles, so that any gases evolved during the reaction may pass through the tube and then into the liquid in the calorimeter.

Solids to be dissolved in liquids in the calorimetor are carefully powdered and sifted, the temperature is approximately determined by surrounding the bulb of the thermometer with the solid, and the substance is rapidly thrown into the calorimeter. Sometimes it is necessary to crush a solid in the calorimeter, (e.g. a deliquescent salt); this is done by means of a little piece of platinum attached to a long thin stem which terminates in a wooden handle. The thermal value of the action of a liquid (e.g. water) on a salt dehydrated by heat is determined by heating the salt in a small weighed flask, cooling in a dry atmosphere, throwing a portion of the salt into the required liquid in the calorimeter, and weighing the salt which remains in the flask.

If the thermal value of an action between a gas and a liquid which absorbs it is to be determined, the tube conveying the pure dry gas into the liquid in the calorimeter is furnished with a three-way stopcock, which is arranged so that the gas passes through the tube for some time and drives out all the air; the stopcock is then turned, and the gas passes into the liquid in the calorimeter. The quantity of gas absorbed can be determined by weighing the calorimeter before and after the experiment, or by analysing the liquid in the calorimeter when the action is completed. The gas is usually allowed to pass until a change of temperature amounting to 2° or 3° has been registered.

The calorimeter which Thomsen employs for measuring the thermal values of reactions between liquids which do not readily evaporate, or evolve gases during their mutual action, consists of two platinum vessels, placed one at a higher level than the other[1]. The capacity of the upper vessel (*A* fig. 3) is 500 c.c.; that of the lower (*B* fig. 3) being 1000 c.c. Each is surrounded by an outer vessel (*C* and *D* fig. 3), and each is furnished with a stirrer (*c* and *c'*) and a thermometer (*t* and *t'*), and is covered by a lid. Communication between the two vessels is established by means of a short platinum tube (*d*),

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[1] *Thermochemische Untersuchungen* **1.** 18—24.

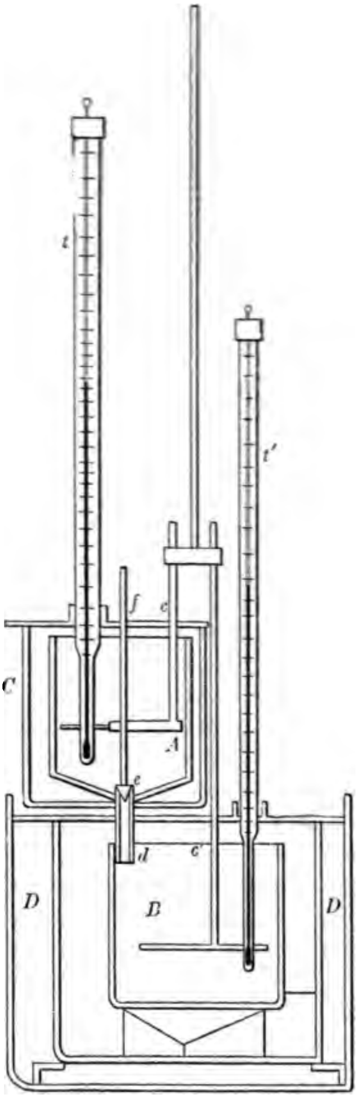

FIG. 3.

stopped at its upper end by a plug of platinum (*e*); this plug can be removed by raising a platinum rod (*f*) which passes through the cover of the upper vessel of the calorimeter. The liquids which are to be mixed are weighed out into the two vessels, the stirrers are set in motion, and the temperature of each liquid is noted at regular intervals. When the temperatures are the same the platinum plug is withdrawn; the liquid in the upper vessel flows rapidly into the lower vessel (the stirrer being in motion); and the course of the thermometer in the lower vessel is noted for some time (from 3 to 6 minutes).

Thomsen surrounds his calorimeter proper with one outer vessel only; the temperature of the room in which he works does not vary more than 0°·1 to 0°·2, during the time he daily devotes to his experiments[1].

B. Calorimeters for measuring the thermal values of processes of combustion, or of reactions between liquids, or liquids and solids, wherein much heat is evolved; e.g. combustion of hydrogen in chlorine, action of nitric acid on benzene or on cellulose.

For measuring the thermal value of the combustion of hydrogen in chlorine, Thomsen employs a platinum bulb of about 500 c.c. capacity (*A* fig. 4), placed in a vessel containing 3000 grams of

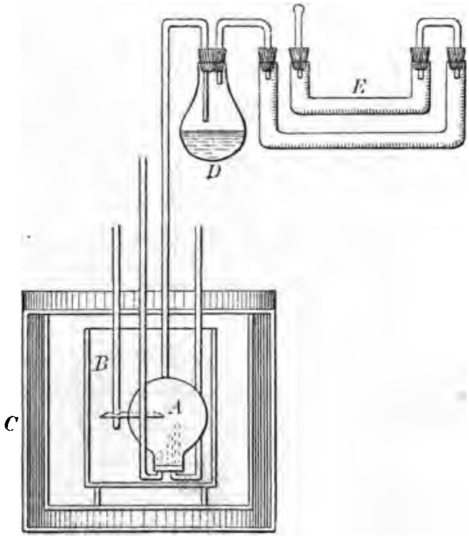

FIG. 4.

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[1] For a description of the room and the methods used for maintaining a constant temperature, see Thomsen, *loc. cit.* **1.** 22—24.

water (*B* fig. 4), itself surrounded by a larger vessel with double walls the space between which is filled with water (*C* fig. 4). Pure dry hydrogen and chlorine flow at a definite and constant rate[1] into the platinum bulb (*A*); the combustion is started by the passage of an induction-spark between two thin platinum wires on either side of the opening of the tube which delivers chlorine. A third tube conducts away the hydrochloric acid which is formed, into water contained in a flask and two tubes (*D* and *E* fig. 4), which are weighed before and after each experiment. The solution of hydrochloric acid formed in the absorption-apparatus is carefully analysed after each combustion. The calorimeter (*B*) and the outer vessel (*C*) are each furnished with a stirrer and a thermometer.

Berthelot determines the thermal value of such reactions as that which occurs when sulphur is burnt in oxygen, or when hydrogen is burnt in oxygen or in chlorine, in a calorimeter consisting essentially of a cylindrically shaped vessel of thin hard glass of about 400 c.c. capacity, surrounded by about 1000 c.c. water contained in a calorimeter of platinum with its surroundings of outer vessels as described on p. 29.

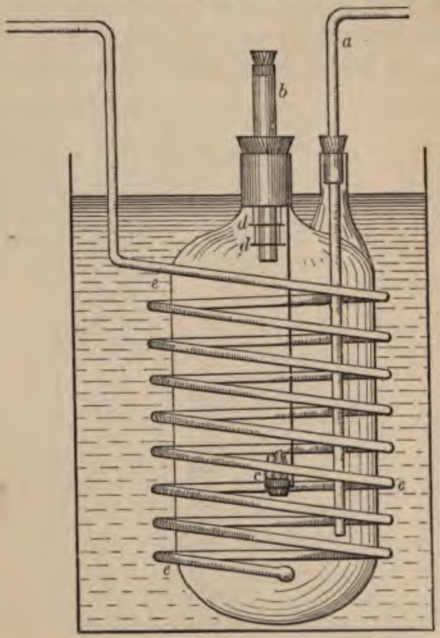

FIG. 5.

[1] Those parts of the apparatus for making and purifying hydrogen and chlorine are not shewn in fig. 4: for details, which are very complicated, see Thomsen *loc. cit.* **2.** 8—18.

Fig. 5 represents the apparatus. The glass vessel has two necks. Oxygen (or whatever the gaseous supporter of the combustion may be) enters by the tube *a* which passes through the narrower neck. The wider neck is fitted with a cork through which passes a glass tube *b*; the small porcelain crucible *c* is suspended by a platinum wire immediately underneath the centre of the tube *b*. Plates of mica (*d*, *d*) protect the cork from being scorched during the reaction.

Near the bottom of the glass vessel is an opening from which proceeds the glass spiral tube *e*, *e*, *e*; the gaseous products of combustion pass away through this spiral after being cooled by the water in the calorimeter.

The combustion of sulphur and of certain solid hydrocarbons in oxygen is described in detail by Berthelot[1]. The combustion of sulphur is started by dropping a small piece of burning charcoal through the tube *b* into the crucible *c* which contains the sulphur. Special arrangements are described for condensing and measuring the sulphur dioxide (and small quantity of carbon dioxide) produced. In the combustion of a solid hydrocarbon the crucible *c* is replaced by a small metallic lamp, with a wick of asbestos, containing the hydrocarbon, which is ignited just as the lamp is introduced into the glass vessel. The carbon dioxide and water produced are collected by special methods; traces of unburnt hydrocarbon are collected and weighed.

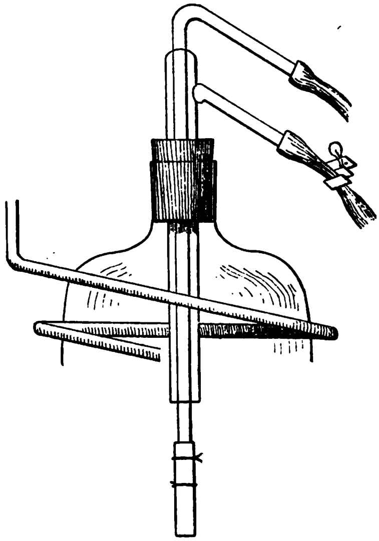

FIG. 6.

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[1] *Mécanique Chimique* 1. 242—246.

When a gas is burnt in a gas (e.g. hydrogen in chlorine) the glass vessel is made with one neck, through which passes a cork, carrying two delivery tubes, arranged as shewn in fig. 6. The ends of these tubes within the glass vessel are made of thin platinum foil.

For measuring the thermal change which accompanies the action of concentrated nitric acid on benzene, mannite, cellulose, &c. Berthelot employs a small platinum cylinder of a capacity of about 60 c.c. immersed in about 600 c.c. water, contained in a calorimeter with surrounding vessels &c. such as has been already described. A weighed quantity of nitric acid is placed in the small platinum cylinder, the water is kept in motion until the temperature is constant, and the benzene is then added drop by drop, with constant agitation both of the cylinder and the exterior water. If the body to be nitrated is a solid, e.g. cellulose, a weighed quantity is placed in the cylinder, which is closed by a cork covered with paraffin, and the acid and cellulose, or other body, are brought into close contact by stirring with a small glass rod.

Berthelot describes a *petit laboratoire* of platinum, for use in reactions wherein gases or volatile liquids take part. The dimensions of this vessel (see fig. 7) are such that it may be placed in the midst of about 600 c.c. water contained in one of Berthelot's ordinary calorimeters. The apparatus consists of three parts; a cylinder *A*, *A*, of a capacity of about 50 c.c.; a spiral tube *B*, *B*, *B*; and a receiver *C*. The spiral tube passes into a side tube soldered on to the cylinder a little way beneath the point where the latter is narrowed; this spiral also fits firmly, but so that it may be withdrawn when required, into a tube soldered into the side of the receiver. Sheet caoutchouc is wrapped round the points of junction of the spiral and the side tubes of the cylinder and receiver.

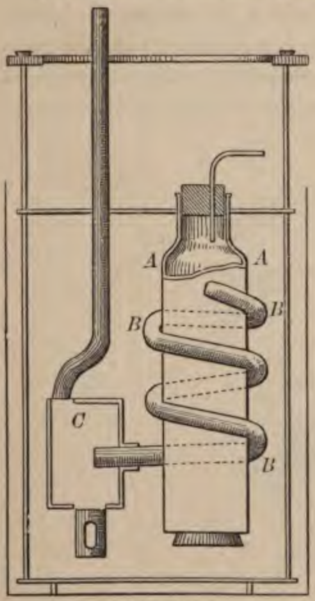

FIG. 7.

C. Special calorimeters for measuring the thermal values of various chemical changes.

When a reaction occurs without explosive violence between two gases at ordinary temperatures, e.g. $NO + O = NO_2$, Berthelot frequently makes use of two glass bulbs, one placed inside the other. The smaller bulb is blown very thin in one or two places; it is filled with one of the gases, and is placed inside the larger bulb. The outer bulb is then drawn out to a fine opening at one end, filled with the other gas, and sealed. The whole arrangement is fixed on a stirrer and immersed in water in a calorimeter; the inner bulb is broken by briskly agitating the larger bulb, and the course of the thermometer in the calorimeter is noted. The larger bulb is now turned so that its drawn-out end is downwards, a solution of some reagent which will absorb the products of the chemical action is added to the water in the calorimeter, and the end of the bulb is broken. The liquid is then collected and analysed. Fig. 8 shews the bulbs $\frac{1}{3}$ actual size.

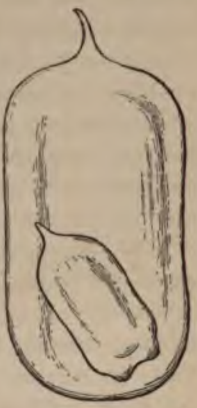

FIG. 8.

When the thermal change which is to be measured is the accompaniment of a chemical change occurring at a slow rate between a gas and a liquid, e.g. the action of ozone on arsenious oxide solution, or when the liquid used is changed by exposure to air, e.g. sodium hyposulphite solution, a closed calorimeter must be employed and special precautions must be taken.

As typical cases let us glance at Berthelot's methods for determining the thermal value of the action between ozone and arsenious oxide solution, and of the action between oxygen and an aqueous solution of sodium hyposulphite.

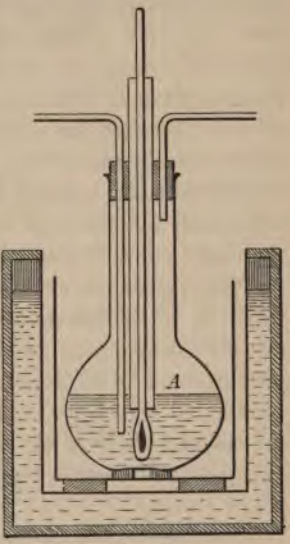

FIG. 9.

The apparatus in which the first of these reactions is conducted is shewn in fig. 9. Ozonised oxygen passes into the flask *A*, the capacity of which is 800 c.c., and which contains 600 c.c. of an aqueous solution of arsenious oxide, to which about 5 c.c. of concentrated hydrochloric acid has been added. The arrangement of entrance and exit tubes, thermometer &c. is sufficiently indicated by the figure; the flask is shewn placed inside one of Berthelot's ordinary calorimeters. The passage of ozonised oxygen is continued for 20 to 30 minutes, the rise of temperature being continuously noted. The electric discharge is now stopped, but the passage of oxygen is continued for 20 minutes longer. The contents of the flask are now analysed (by titration with standardised permanganate solution); a similar analysis is made of 600 c.c. of the original arsenious oxide solution, and so data are obtained for finding the quantity of arsenious oxide oxidised to arsenic oxide, and hence for finding the mass of ozone absorbed by the solution[1].

The absorption of oxygen by sodium hyposulphite solution is conducted in an apparatus closely resembling that shewn in fig. 9. About 650 c.c. of an aqueous solution of the hyposulphite is used, the concentration being such that this quantity can absorb about six times its volume of oxygen. At the beginning of the experiment the flask is filled with nitrogen by displacement; the hyposulphite solution is then run in from a specially constructed reservoir, the atmosphere in which consists of nitrogen; the entrance and exit tubes of the flask are closed by small caps, and the flask and its contents are weighed. The flask is then placed inside the silver vessel of a large calorimeter, and the course of the thermometer is observed for 10 minutes; a tube which conveys pure dry oxygen from a gas holder is attached to the entrance tube of the flask; the exit tube from the flask is attached to another tube passing under the surface of water so that the rate of the oxygen-current may be regulated, and oxygen is passed into the solution in the flask. The course of the thermometer is noted for 10 minutes or so; the stream of oxygen is stopped, and the caps are placed on the entrance and exit tubes of the flask, which is again weighed.

When gases are evolved during a reaction the thermal value of which is to be determined, and when it is necessary to collect and measure these gases in the calorimeter, complicated forms of apparatus must be employed.

Fig. 10 represents the arrangement made use of by Berthelot for the thermal study of the action of an aqueous solution of potash on an aqueous solution of hydroxylamine hydrochlorate ($\dot{N}H_2OH\ HCl$).

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[1] The ozoniser used by Berthelot is not shewn in the figure. It is a useful piece of apparatus; see for a description *Mécanique Chimique* **1.** 222—224. Cup-joints containing sulphuric acid are better than those described by Berthelot.

The reaction in question results in the formation of potassium chloride, ammonia, nitrogen, and water; in order to determine the amount of chemical change accompanying a measured thermal change

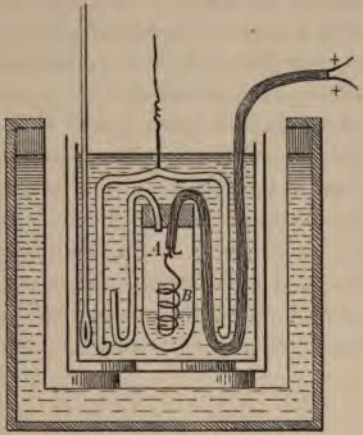

FIG. 10.

it is necessary to collect and measure the nitrogen which is formed. The large test tube *A* contains a known quantity of an aqueous solution of potash of known strength; the smaller tube *B* contains about 1 gram of a concentrated aqueous solution of hydroxylamine hydrochlorate. The small tube is held in the position shewn by a spiral of thick platinum wire, which is attached by a very thin short piece of platinum wire ($\frac{1}{20}$th millim. thick) to the ends of two copper wires covered by caoutchouc so as to form an electric cable which passes out of the calorimeter to a battery. The tubes *A* and *B* are arranged inside a glass bell-jar capable of containing 200 to 250 c.c. water, and this is itself placed in a large calorimeter containing about 1000 c.c. water. The bell-jar fits into an exterior covering of copper to which a handle is attached; by this means the bell-jar with the tubes can be firmly fixed in the water of the calorimeter. The tube *A* is closed by a cork, through which pass the electric wires, and also an exit tube for the gas produced during the reaction. Every part of the apparatus is weighed separately before the experiment begins; the specific heat of each part is of course determined. The bell-jar with its contents having been lowered into the calorimeter and secured, the air in the jar is removed by means of an inverted syphon; the course of the thermometer in the calorimeter is observed for 10 minutes; an electric current is passed for an instant, whereby the small thin platinum wire is melted, the tube containing the hydroxylamine salt drops into the larger tube containing potash, and the chemical reaction proceeds. When no more gas has been evolved for some time, the calorimeter and its contents are placed in a large vessel full of water; the calorimeter is removed; and the gas in the bell-jar is transferred to a measuring vessel, where its volume is determined.

The volume of air in the tubes *A* and *B* is known from preliminary experiments; hence the volume of nitrogen produced in the reaction is found, and hence the amount of chemical change which has accompanied the observed thermal change is calculated.

It is sometimes necessary to add a definite quantity of heat to the chemical system under consideration in order to bring about the change the thermal value of which is to be determined.

Take for instance Berthelot's determination of the thermal value of the reaction

$$NH_4 NO_2 = N_2 + 2H_2 O,$$

occurring at about 80°.

The apparatus consists essentially of two parts: one designed for the purpose of adding an accurately measured quantity of heat to

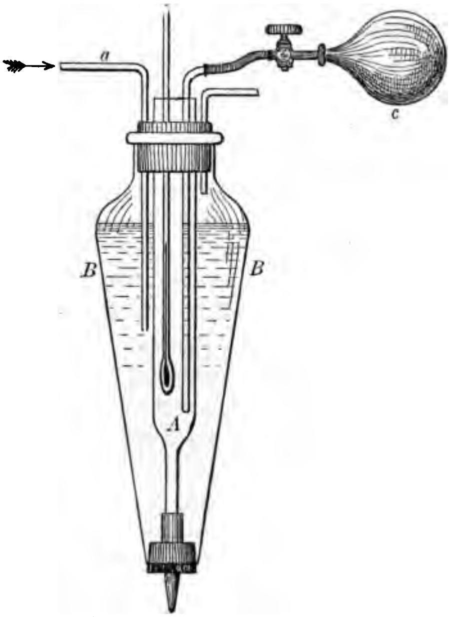

FIG. 11.

a known quantity of ammonium nitrite; another designed for the purpose of measuring the quantity of heat evolved (or absorbed) during the decomposition of this quantity of ammonium nitrite. The source of heat is 25 grams of water at a definite temperature.

This mass of water is placed in the inner tube *A* of the apparatus shewn in fig. 11. This tube is surrounded by a considerably larger vessel, *BB*, containing about 800 c.c. water, which is heated by passing steam into it by the tube *a*. When the temperature of the 25 grams of water in the tube *A* is a very little higher than the desired temperature, a few bubbles of air are passed into the water by pressing the caoutchouc ball *c*; the thermometer is again read; a mark is made by a sharp file close to the lower end of *A*; and the whole apparatus is transferred to the vessel containing the ammonium nitrite to be decomposed. This apparatus is represented in fig. 12. It consists of three large tubes of thin glass, *AA*, *aa*, and *BB*, placed inside a calorimeter containing about 800 c.c. water. The tube *aa* is a very little wider than *AA*; the space between them is partly occupied by a concentrated aqueous solution (about 3—4 c.c.) of

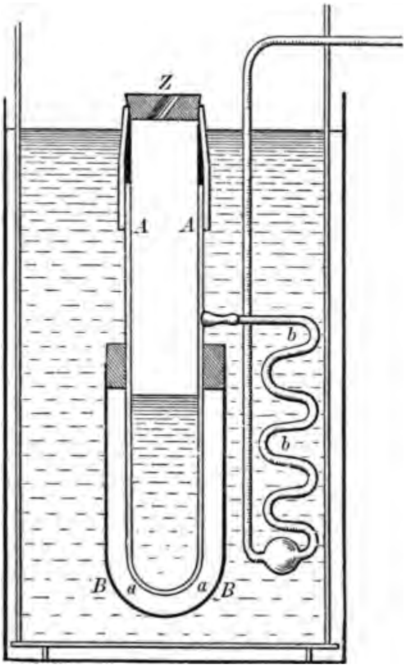

FIG. 12.

ammonium nitrite, the upper level of this liquid being a little lower than the level of the warm water in the inner tube *AA*.

A hole (*Z*) is made in the cork which closes *AA*; the lower end of the tube containing the 25 grams of warm water is inserted through this hole; the point of the tube is broken off by pressing against the side of the tube *AA*; the water rushes into *AA*, and the chemical reaction begins. The gaseous products of decomposition pass through the spiral tube *bb*, and, after being cooled, are collected in a graduated tube. The space between the tubes *aa* and *BB* is filled with air; this prevents the cold water in the calorimeter from lowering the temperature of the ammonium nitrite solution and so stopping the decomposition. The quantity of ammonium nitrite remaining when the action has ceased is determined. Two experiments must be made, one to find the rise of temperature in the water of the calorimeter produced by running in the 25 grams of warm water, and the other to determine the total rise of temperature which occurs when the water is run in, and the chemical action is thereby accomplished.

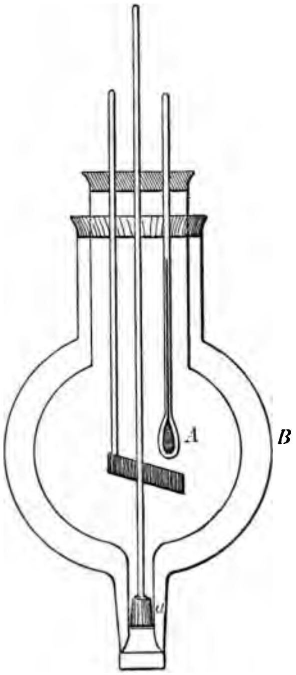

FIG. 13.

Sometimes it is desired to determine the thermal value of an operation which occurs at a temperature higher than that of the surrounding air, and which must be conducted in a chamber surrounded by a medium hotter than the exterior air. For instance, let it be required to measure the quantity of heat evolved or absorbed when common salt dissolves in water at 86°. Berthelot conducts the operation in a glass vessel placed inside another similarly shaped larger vessel; the space between the vessels is filled with air, and the outer vessel is immersed in hot water: see fig. 13. A weighed quantity of finely powdered salt is placed in *A*; when the temperature of *A* and that of the water in which the whole apparatus is immersed are both at 86°, and have remained constant for some time, the glass plug *a* is lifted, the stirrer is set in motion, and the course of the thermometer, as also that of a thermometer in the water outside *B*, is noted[1].

50. In many of the methods described in the preceding paragraph the heat which is produced in a specified chemical operation is used in raising the temperature of the chemically reacting liquids. In other cases most, or all, of the heat is used in raising the temperature of a quantity of water. Before the thermal values of the former class of reactions can be found it will evidently be necessary to make very careful measurements of the specific heats of the liquids employed, and of those produced in the reactions.

The specific heat of a body under any specified conditions, is the number of gram-units of heat required under these conditions to raise the temperature of 1 gram of that substance through 1° C, the gram-unit of heat being defined as the quantity of heat required to raise the temperature of 1 gram of water from 0° to 1° C.

Consider such a case as the mutual action of caustic soda and sulphuric acid in aqueous solution. Determinations must be made of the specific heats of aqueous solutions of various concentrations of (1) caustic soda, (2) sulphuric acid, (3) sodium sulphate, (4) sodium-hydrogen sulphate; these determinations must be made for a moderate range of temperature. Such determinations have been conducted by various observers; more recently and accurately by Thomsen. The method adopted by Thomsen is to raise the temperature of each specified liquid by using a source of heat which has been thoroughly investigated, and is thoroughly under control. A definite volume of pure hydrogen is burnt in oxygen in a chamber made of thin sheet copper, thickly gilded, placed in a calorimeter capable of containing 1000 c.c. of water. About 900 c.c. of the saline solution to be examined is placed in this calorimeter, and the rise of temperature is noted from time to time. As the quantity of heat produced by the burning of the hydrogen is known, the specific heat of the given solution can be calculated. Very great precautions are taken by Thomsen to have the hydrogen and oxygen pure, and to make sure that the flow of each gas proceeds at a uniform rate during the experiment[1]. From a series of such determinations the value of the specific heat of each liquid is deduced for certain specified temperatures[2].

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[1] For descriptions of other special forms of calorimetric apparatus, and for more details regarding those sketched in this paragraph, see Berthelot *loc. cit.* 1. 217—274: also Id. *La Force des Matières Explosives*, 1. 227—231.

When the rise of temperature in the known mass of water, or in the known mass of saline or other solution in the calorimeter has been determined, the initial temperature of the water or other liquid being known, the thermal value of the given reaction is found by applying the ordinary formula

$$r = ms\,(T - t),$$

where m = mass of liquid with specific heat s, T = final, and t = initial temperature.

This formula must be amplified according to the circumstances of the special experiments. The water-equivalent of the calorimeter (including the glass or other apparatus and the thermometer immersed in it) must be determined, i.e. the number of units of mass of water the temperature of which would be changed by the heat evolved in the reaction to the same extent as the given mass of calorimeter &c., must be determined.

Let us suppose the heat of neutralisation of sulphuric acid by caustic soda is to be determined. Let dilute solutions of these two compounds be prepared containing equivalent quantities, in grams, of the alkali and the acid in known quantities of water; the total mass of each solution is therefore known. The temperature of each liquid having been determined, let the liquids be mixed and the rise of temperature noted. Let the water-equivalent of the calorimeter and thermometer be determined, and also let the specific heat of the liquid produced by mixing the two compounds (i.e. the specific heat of aqueous sodium sulphate solution of a certain degree of concentration) be known. Then, putting the initial temperature of the soda solution whose mass is m, as equal to t, the initial temperature of the acid solution whose mass is m_1, as equal to t_1, we may say that the mean initial temperature of the two liquids is $\frac{t+t_1}{2}$ (as t and t_1 are almost identical). Further, let the final temperature of the mixed liquids $= t_2$; let the mean specific heat of this liquid for the temperature-interval $t_2 - \frac{t+t_1}{2}$ be equal to s; and let the water-equivalent of the calorimeter &c. $= c$. The formula for finding the thermal value of the reaction is then

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[1] For a full description of Thomsen's methods of procedure see his *Untersuchungen* **1.** 25—35.

[2] For details of the calculation see Thomsen, *loc. cit.* **1.** 35.

$$r = (m + m_1)\, s \times \left(t_2 - \frac{t+t_1}{2}\right) + c\left(t_2 - \frac{t+t_1}{2}\right).$$ [1]

SECTION II. *Methods of stating the results of thermochemical measurements.*

51. The notation adopted in thermal chemistry is simple. The chemical formulæ of the reacting substances are enclosed in a square bracket; a comma, or sometimes a colon, placed between two formulæ means that the quantities of the substances represented by these formulæ react chemically on each other. The sign of equality is used to express the fact that the chemical change represented is accompanied by the production or absorption of a certain number of units of heat. The sign + is placed after the number expressing the quantity of heat if this quantity of heat is evolved, the sign − is placed in a similar position if this quantity of heat is absorbed, during the chemical change.

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[1] For Thomsen's development of this formula see *loc. cit.* **1.** 20—21. See also Berthelot *loc. cit.* **1.** 187—214. See also *post* pars. 55, 56, 57.

If no sign is placed after the number expressing the quantities of heat, the + sign is to be understood. The indices attached to the elementary symbols in chemical formulæ may be written either above or below these symbols. Thomsen always writes them above, when he is dealing with thermochemical changes. His example is followed in this book. Thus $[H^2, O] = 68{,}360 +$, means that when 2 grams of hydrogen combine with 16 grams of oxygen, at the ordinary pressure and under such conditions that the temperature of the surroundings does not vary from 18°—20°, with formation of 18 grams of water at the same temperature, a quantity of heat is evolved which suffices to raise the temperature of 68,360 grams of water at 18°—20° C, through one degree centigrade.

Again $[NH^3, HCl] = 41{,}900 +$ means, that when 17 grams of ammonia gas combine with 36·5 grams of hydrochloric acid gas, at the temperature of 18—20° and the ordinary pressure, with formation of 53·5 grams of ammonium chloride, a quantity of heat is evolved which if transferred to 41,900 grams of water at 18°—20° would raise the temperature of that water through one degree centigrade.

The symbol Aq is employed to represent a large quantity of water: the symbol H^2O represents 18 grams of water.

Thus $[HCl, Aq] = 17{,}320 +$ means, that 17,320 gram-units of heat are produced when 36·5 grams of gaseous hydrochloric acid are absorbed and dissolved, at the temperature of 18°—20° and the ordinary pressure, by a quantity of water so large that an increase in this quantity would not affect the thermal value of the reaction. Again $[H, Cl, Aq] = 39{,}300 +$ means, that 39,300 gram-units of heat are evolved when 1 gram of hydrogen combines with 35·5 grams of chlorine and the product dissolves in a large excess of water.

Again compare these equations,

(1) $[SO^2, O, H^2O] = 53{,}480 +$: (2) $[SO^2, O, Aq] = 71{,}330 +$.

The first represents the number of gram-units of heat evolved when 64 grams of sulphur dioxide, 16 grams of oxygen, and 18 grams of water combine to form 98 grams of liquid sulphuric acid at 18°—20°; the second represents the number of gram-units of heat evolved when 64 grams of sulphur dioxide, 16 grams of oxygen, and 18 grams of water combine to form 98 grams of sulphuric acid, and the product at the same time dissolves in a large excess of water.

When a compound is separated into its constituent parts the equation representing the change is preceded by the minus sign. Thus $-[H, Cl] = -22{,}000$ means, that 36·5 grams of hydrochloric acid gas are decomposed, by some means, into 1 gram of hydrogen and 35·5 grams of chlorine, and that this chemical change is accompanied by absorption of 22,000 gram-units of heat. Such a separation into parts is usually, but not always, accompanied by absorption of heat.

52. A chemical reaction between a compound and an element, or between two compounds, may be always regarded from the thermal point of view as consisting of two stages; (1) separation of the original compound, or compounds, into parts, (2) re-combination of these parts to produce the new compounds.

Thus, the change represented by the equation

$$NH_3 + HCl = NH_4Cl,$$

if analysed from the thermal standpoint will be represented thus

$$[NH^3, HCl] = -[N, H^3] - [H, Cl] + [N, H^3, H, Cl].$$

That is, the total thermal change consists in (1) the separation of 17 grams of ammonia into 14 grams of nitrogen + 3 of hydrogen; (2) the separation of 36·5 grams of hydrochloric acid into 35·5 of chlorine + 1 of hydrogen; and (3) the combination of these several quantities of nitrogen, hydrogen, and chlorine to produce 53·5 grams of ammonium chloride.

The reaction of iron on a dilute aqueous solution of copper sulphate is represented thus

$$CuSO_4\,Aq + Fe = FeSO_4\,Aq + Cu.$$

Thermally considered, this change would be written

$$[CuSO^4\,Aq, Fe] = -[Cu, SO^4\,Aq] + [Fe, SO^4\,Aq].$$

The formation of lead sulphide by the action of sulphuretted hydrogen on lead oxide when set down in the ordinary chemical notation stands thus

$$PbO + H_2S = PbS + H_2O.$$

When this equation is expanded from the thermal point of view, it appears in this form

$$[\mathrm{PbO}, \mathrm{H}^2\mathrm{S}] = -[\mathrm{Pb}, \mathrm{O}] - [\mathrm{H}^2, \mathrm{S}] + [\mathrm{Pb}, \mathrm{S}] + [\mathrm{H}^2, \mathrm{O}].$$

53. Generally then, let r = the number of gram-units of heat evolved or absorbed during a definite chemical change; then we have these five cases[1]:—

(1) A definite amount of a compound, $X_a\ Y_b\ Z_c$, is produced by the combination of a grams of X, b grams of Y, and c grams of Z; then

$$r = [X^a, Y^b, Z^c].$$

(2) The same quantity of the same compound is produced in presence of a large excess of water in which it is dissolved; then

$$r = [X^a, Y^b, Z^c, \mathrm{Aq}].$$

(3) The same quantity of the same compound is dissolved in a large excess of water; then

$$r = [X^a\ Y^b\ Z^c, \mathrm{Aq}].$$

(4) The compound XY is decomposed by the element Z, with production of the new compound XZ and the element Y; then

$$r = [XY, Z] = [X, Z] - [X, Y].$$

(5) The compound XY is decomposed by the compound VZ with production of the two new compounds XZ and VY; then

$$r = [XY, VZ] = [X, Z] + [V, Y] - [X, Y] - [V, Z].$$

54. The quantity of heat evolved or absorbed during a definite chemical reaction will vary with variations in the temperature at which the reaction occurs, in the state of aggregation of the constituents of the changing system, and in the volume occupied by these constituents, and with variations in the pressure to which the system is subjected during the change.

Thomsen and Berthelot have independently investigated the influence of temperature-changes on the quantity of heat evolved or absorbed during a definite chemical reaction.

55. Such a statement as [HCl Aq, NaOH Aq] = **13,500** +, only holds good when the temperature both of the initial and

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[1] Thomsen, *Thermochem. Untersuch.* **1.** 5 *et seq.*

the final system is 18—20° C. If it is desired to find the value of the same reaction at some other temperature, it will be necessary to determine the specific heats of the reacting substances, and the specific heat of the product of the reaction; since the specific heat of any substance varies as temperature varies. The variation in the case of water is very small; thus according to Regnault's investigations[1] the specific heat of water at any temperature, t, may be found by the formula

$$\text{spec. heat} = 1 + \cdot 000{,}04\, t + \cdot 000{,}000{,}9\, t^2.$$

Many determinations have been made of the specific heats of aqueous solutions of acids, alkalis, and salts, and of various liquid compounds[2].

If two liquids, the masses of which are represented by A and B, chemically react to produce the liquid AB, and if the specific heat of $A = \alpha$, of $B = \beta$, and of the product $AB = \gamma$, then the *calorimetric equivalents* of the three liquids are

$$A.\alpha = q_a,\ B.\beta = q_b,\ AB.\gamma = q_c.$$

If the chemical reaction proceeds at two temperatures, T and t, which are not far apart from each other, we may conclude, without introducing a sensible error, that the values of α, β, and γ, and therefore the values of q_a, q_b, and q_c, are independent of the temperature.

Then, putting the heat evolved during the reaction when it proceeds at the higher temperature T as R_T, and the heat evolved during the same reaction when it proceeds at the lower temperature t as R_t, it can be shewn from the second law of thermodynamics that

$$R_T - R_t = (T - t)\ (q_a + q_b - q_c)^3;$$

and hence the variation in the value of R for each degree of temperature, ϕ, can be found by the equation

$$\phi = \frac{R_T - R_t}{T - t} = q_a + q_b - q_c.$$

Then, if the value of R at 0° is R_0, the value of R at a temperature t not far removed from 0° (i.e. the value of R_t) can be found when ϕ is known; for

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[1] *Mém. de l'Acad.* **21.** 729 *et seq.* For more details see Naumann's *Thermochemie*, 269—272; or Landolt and Börnstein's *Physikalisch-Chemische Tabellen*, 176.

[2] For details and data see Naumann *loc. cit.* 269—309.

[3] See Thomsen *loc. cit.* **1.** 65—66.

$$R_t = R_0 + \phi t.$$

These formulæ are applicable only when the difference $T - t$ is small, and when it may be assumed that the variations in the values of the specific heats of the various liquids are independent of the temperature. A general formula could be applied only when the relation between the specific heat and the temperature of each solution, and also the relation between the variation in the value of the calorimetric equivalent and the composition of each solution, were completely known[1].

56. If the chemical change, the thermal value of which is to be determined, is accompanied by a change of the state of aggregation of some of the constituents of the system, then not only must the specific heats of the various constituents at different temperatures be known, but measurements must also be made of the quantities of heat absorbed or evolved in the changes from solid to liquid, and liquid to gas, or *vice versa*, which occur.

57. The following example illustrates the nature of the determinations and calculations required[2].

If 4 grams of hydrogen at $18^\circ - 20^\circ$ combine with 32 grams of oxygen at the same temperature, to produce 36 grams of liquid water at 18°—20°, there are evolved 136,720 gram-units of heat. How much heat will be evolved if the same masses of hydrogen and oxygen combine at the temperature of 200°, and the product of the combination is maintained at this temperature, the pressure being constant?

Let U = the quantity of heat, measured in gram-units, which is required to raise the temperature of the initial system ($2H_2 + O_2$ grams) from 18° to 200°; and let V = the quantity of heat which is required to raise the temperature of the final system ($2H_2O$ grams) through the same temperature-interval. Further let Q_{200} = the quantity of heat evolved when the chemical reaction proceeds at 200°, and Q_{18} = the quantity of heat evolved when the reaction proceeds at 18°.

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[1] Such a formula can be obtained; see Thomsen *loc. cit.* **1.** 66. For a discussion of the connections between the specific heats, the composition, and the volumes, of saline solutions see Id. *loc. cit.* **1.** 60—78.

[2] See Naumann, *loc. cit.* 212—213.

$$\text{Then } Q_{200} = Q_{18} + U - V.$$

To find U we have the following data.

$$\left.\begin{array}{l}\text{Specific heat of hydrogen} = 3{\cdot}409 \\ \quad ,, \quad ,, \quad \text{oxygen} = 0{\cdot}2175\end{array}\right\} \text{(at constant pressure)}$$

∴ (as 200 − 18 = 182), 4 × 182 × 3·409 = quantity of heat required to raise the temperature of the hydrogen in the initial system through the given temperature-interval,
= 2,481 gram-units;

and 32 × 182 × ·2175 = quantity of heat required to raise the temperature of the oxygen in the initial system through the given temperature-interval,
= 1,266 gram-units;

∴ U = 3,747 gram-units of heat.

To find V we have the data.

Specific heat of water = 1; heat of vaporisation of water = 536·5.

Specific heat of water gas = ·4805 (at constant pressure, for temperature-interval 128 − 217°).

∴ (as 100 − 18 = 82), 36 × 82 × 1 = quantity of heat required to raise the temperature of the water produced in the reaction from 18° to 100°;
= 2,952 gram-units;

and 36 × 536·5 = quantity of heat required to convert the water at 100° into steam at 100°;
= 19,314 gram-units;

and 36 × 100 × ·4805 = quantity of heat required to raise the temperature of the steam from 100° to 200°;
= 1,730 gram-units;

∴ V = 23,996 gram-units of heat.

Hence Q_{200} = 136,720 + 3,747 − 23,996 = 116,471 gram-units of heat.

When a salt is dissolved in water, or when aqueous solutions of two salts are mixed, very considerable contraction frequently occurs. This is attended with production of heat; hence the thermal values of many chemical changes occurring between bodies in solution vary with variations in the volumes of the reacting solutions[1]. Contraction of volume also generally occurs when gaseous elements or compounds combine to form gaseous products; in such cases heat is produced, and the quantity of this heat must be ascertained and taken into account in calculating the thermal value of the chemical reaction[2].

SECTION III. *Heats of combustion, and of formation, of compounds.*

58. The *heat of combustion* of an element or compound is the quantity of heat produced during the complete oxidation of that element or compound to form those masses of the products of oxidation which are represented by the chemical formulæ of these products[3].

The *heat of formation* of a compound is the quantity of heat evolved, or absorbed, during the formation of the mass of the compound represented by its formula, from those masses of the constituents of the compound which are represented by the formulæ of these constituents.

When a compound can be oxidised, then the heat of formation of that compound is the difference between the sum of the heats of combustion of its constituents and the heat of combustion of the compound itself. The constituents may be the elements by the putting together of which the compound is produced, or they may be groups of elements which combine to form the compound in question. Thus 98 grams of sulphuric acid may be formed by burning 32 grams of sulphur in oxygen in the presence of nitrogen trioxide and of 18 grams of water, or the same mass of the same acid may be formed by passing 64 grams of sulphur dioxide, mixed with an excess of oxygen, over hot spongy platinum, and dissolving the 80 grams of sulphur trioxide thus produced in 18 grams of water. The former reaction would be represented in chemical symbols thus,

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[1] This subject will be considered in more detail in a future chapter. See post, par. 198.

[2] See Thomsen, *loc. cit.* 2. 101—102.

[3] In accordance with this definition, the *heat of combustion* of hydrogen is the quantity of heat produced in the reaction $H_2 + O = H_2O$, and not the quantity produced by burning 1 gram of hydrogen.

$$S + O_2 + O \text{ (supplied by nitrogen oxide)} + H_2O = H_2SO_4\,;$$

the latter thus,

$$SO_2 + O + H_2O = H_2SO_4.$$

In the notation of thermal chemistry the two reactions would be written thus,

$$(1)\ \ [S, O^2, O, H^2O]\,;\quad (2)\ \ [SO^2, O, H^2O].$$

The heat of formation of sulphuric acid would be represented by a different number according as the formation was accomplished from the elements sulphur and oxygen and the compound water, or from the element oxygen and the compounds sulphur dioxide and water. If however the formation of the acid is accomplished from the elements hydrogen, oxygen, and sulphur, the value of the 'heat of formation' is the same whether these elements directly combine to produce the acid, or whether oxides of sulphur and of hydrogen are first produced and then mutually react to form the acid.

59. The deduction from the principle of the conservation of energy, of which the statement just made regarding the heat of formation of sulphuric acid is a special example, underlies all the calculations of thermal chemistry. The deduction in question is to the effect that the change of energy which accompanies the passage of a system from one definite state to another is independent of the intermediate states through which the system may pass. (See *ante*, par. 16.)

60. We shall now give some illustrations of the methods by which the heats of formation of compounds are determined.

It must be remembered that by the heat of formation of a compound is meant the heat of formation of that mass of the compound which is expressed by the chemical formula of the compound. Except in a few cases, which will be specially mentioned, we shall use the formula of an element or compound as representing a certain number of grams of the body.

I. Required the heat of formation of methane, CH_4, from carbon and hydrogen.

Data:

$$\left.\begin{array}{r}\text{(1) heat of combustion of carbon } [C, O^2] = 96{,}960,\\ \text{(heat of combustion of hydrogen)} \times 2 \text{ i.e. } 2\,[H^2, O] = 136{,}720,\end{array}\right\} = 233{,}680.$$

(2) heat of combustion of methane $[CH^4, O^4]$.............. = 211,930.

Difference = 21,750.

Therefore the heat of formation of $CH_4 = 21{,}750$ gram-units +.

In obtaining data (1) and (2) the final configuration of the chemical system is the same. Thus the reactions represented as $[C, O^2]$ and $2\,[H^2, O]$ when written in the ordinary notation are

$$C + O_2 = CO_2;\ 2H_2 + O_2 = 2H_2O.$$

And the reaction $[CH^4, O^4]$ in the ordinary notation is

$$CH_4 + O_4 = CO_2 + 2H_2O.$$

In one case we start with the system $C + H_4 + O_4$, and we finish with the system $CO_2 + 2H_2O$; in the other case we start with the system $CH_4 + O_4$, which we may suppose to have been produced from the system $C + H_4 + O_4$, and we finish with the system $CO_2 + 2H_2O$. Therefore the difference between the energy-changes accompanying the two chemical changes represents the energy-change attending the formation of the system $CH_4 + O_4$ from the system $C + H_4 + O_4$; but as O_4 occurs in both systems, we say that the energy-change in question is that which accompanies the formation of the system CH_4 from the system $C + H_4$.

At present we shall not say that the change $C + H_4 = CH_4$ represents the formation of one molecule of gaseous methane from one atom of carbon and two molecules of hydrogen, but only that it represents the formation of 16 grams of gaseous methane from 12 grams of solid carbon and 4 grams of gaseous hydrogen. We shall also treat the thermal value of this change, viz. 21,750 gram-units, as representing the complete change, and shall not attempt, at present, to separate it into parts, e.g. the part due to change of solid to gaseous carbon, the part due to rise of temperature or change of volume &c. Our present object is only to illustrate the methods which are employed in finding *heats of formation*, and to give this expression a meaning, which, although it may not be sufficiently wide, is certainly definite.

II. Required the heat of formation of formic acid, CH_2O_2, arbon, hydrogen, and oxygen.

ta:

$$\left.\begin{array}{lr}\text{eat of combustion of carbon,} & [C, O^2] = 96{,}960,\\ \text{,, \quad ,, \quad hydrogen,} & [H^2, O] = 68{,}360,\\ \text{,, \quad ,, \quad oxygen,} & = \quad 0,\end{array}\right\} \overset{\text{sum}}{=165{,}320.}$$

$$(2) \quad \text{,, \quad ,, \quad formic acid, } [CH^2O^2, O] \ldots\ldots = \underline{65{,}900.}$$

$$\text{Difference} = 99{,}420.$$

Therefore the heat of formation of $CH_2O_2 = 99{,}420$ gram-units.

III. Required the heat of formation of the oxides, N_2O and NO, from their elements.

As the element nitrogen cannot be directly burnt in oxygen it is necessary to adopt an indirect method for finding the heats of formation required. Comparing the two reactions,

$$(1) \quad C + 2N_2O = 2N_2 + CO_2,$$

and

$$(2) \quad C + 2N_2 + O_2 = CO_2 + 2N_2,$$

we see that the final systems attained are the same in each case, but in reaction (1) the oxygen needed for burning the carbon has to be separated from its combination with nitrogen, while in reaction (2) no such separation of oxygen from a compound is needed. If the two reactions are expanded thermally[1] they appear thus,

$$(1)\ [C, 2N^2O] = [C, O^2] - 2[N^2, O]\,; \quad (2)\ [C, 2N^2, O^2] = [C, O^2].$$

Hence the difference between the observed values of these two reactions will represent the value of the reaction $-2[N^2, O]$.

The data are:

$$\begin{array}{ll}(1)\ [C, 2N^2O] = [C, O^2] - 2[N^2, O] & = 133{,}900,\\ (2)\ [C, 2N^2, O^2] = [C, O^2] & = \underline{\ \ 96{,}960.}\\ & \text{Difference} = 36{,}940.\end{array}$$

But this difference represents the thermal value of the separation of $2N_2O$ into its elements, therefore the formation of $2N_2O$ from its elements is represented by the negative value $-36{,}940$; and therefore we conclude that the heat of formation of N_2O from its elements $= -18{,}470$ gram-units. The heat of formation of the oxide NO is determined in a similar manner.

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[1] See *ante*, par. 51.

The data are:

$CN + 2NO = CO_2 + 3N$, when expanded thermally becomes

$$[CN, 2NO] = [C, O^2] - [C, N] - 2[N, O] = 174{,}600.$$

$CN + O_2 = CO_2 + N$, when expanded thermally becomes

$$[CN, O^2] = [C, O^2] - [C,N] \ldots\ldots = 130{,}900.$$

$$\text{Difference} = \overline{\;43{,}700.}$$

But the difference represents the thermal value of the transaction $2NO = N_2 + O_2$, therefore $[N^2, O^2] = -43{,}700$; and therefore the heat of formation of NO from its elements $= -21{,}850$ gram-units.

IV. Required the heat of formation of oxalic acid, $H_2C_2O_4$, from its elements. An aqueous solution of oxalic acid is easily oxidised, to water and carbon dioxide, by the action of an aqueous solution of hypochlorous acid. The reaction is formulated thus

$$H_2C_2O_4Aq + HClO\ Aq = H_2O\ Aq + 2\ CO_2 + HCl\ Aq.$$

When expanded thermally this becomes

$$[H^2C^2O^4\,Aq, HClO\ Aq] = [H,Cl, Aq] - [H,Cl,O, Aq] + [H^2C^2O^4Aq, O].$$

The thermal value of this reaction is 71,380 gram-units.

But the value of the difference

$$[H, Cl, Aq] - [H, Cl, O, Aq] \text{ is } 9{,}380 \text{ gram-units};$$

$$\therefore [H^2C^2O^4\ Aq, O] = 71{,}380 - 9{,}380 = 62{,}000.$$

That is to say, the heat of combustion of oxalic acid in aqueous solution $= 62{,}000$ gram-units.

But

$$2[C, O^2] = 193{,}920, \text{ and } [H^2, O] = 68{,}360;\ \text{sum} = 262{,}280;$$

$$\therefore [H^2, C^2, O^4, Aq] = 262{,}280 - 62{,}000 = 200{,}280 \text{ gram-units.}$$

But this last result represents the heat of formation of oxalic acid in aqueous solution. To find the heat of formation of the solid acid $H_2C_2O_4$, the heat-change which occurs when this amount of the acid is dissolved in a large excess of water must be determined. The value in question is

$$[H^2C^2O^4, Aq] = -2{,}256;$$

$$\therefore [H^2, C^2, O^4] = 200{,}280 - (-2{,}256) = 202{,}536 \text{ gram-units.}$$

V. Required the heat of formation of sulphuric acid, H_2SO_4, *from its elements.*

We have here a compound which is already fully oxidised; therefore the heat of combustion of sulphuric acid = 0. But an aqueous solution of sulphur dioxide can be oxidised to sulphuric acid. Let us therefore find the heat of formation of an aqueous solution of SO_2.

The data are:

$$[S, O^2] = 71{,}080;\ [SO^2, Aq] = 7{,}699;$$
$$\therefore\ [S, O^2, Aq] = 78{,}780.$$

But this aqueous solution of SO_2 can be easily oxidised to an aqueous solution of SO_3 by the action of chlorine; the reaction is

$$SO_2Aq + H_2O + Cl_2 = SO_3Aq + 2HCl.$$

When thermally expanded this reaction becomes

$$[SO^2Aq, H^2O, Cl^2] = [SO^2Aq, O] + 2\,[H, Cl, Aq] - [H^2, O].$$

The thermal value of this change is 73,907.

But

$$2\,[H, Cl, Aq] = 78{,}630, \text{ and } [H^2, O] = 68{,}360;\ \text{difference} = 10{,}270.$$
$$\therefore\ [SO^2Aq, O] = 73{,}907 - 10{,}270 = 63{,}637.$$

We have now obtained the thermal values of these two reactions:—

$$(1)\ S + O_2 + Aq = SO_2\,Aq, \text{ and } (2)\ SO_2\,Aq + O = SO_3\,Aq.$$

But it is evident that the sum of these represents the thermal value of the reaction $S + O_3 + Aq = SO_3Aq$.

That is, in thermal notation,

$$[S, O^2, Aq] + [SO^2Aq, O] = [S, O^3, Aq].$$

The value of this reaction is $78{,}780 + 63{,}637 = 142{,}417$.

But this number represents the quantity of heat evolved in the production of a very dilute aqueous solution of sulphuric acid. We must now find how much heat is produced by the formation of (1) SO_3, from its elements; and (2) H_2SO_4, by the action of H_2O on SO_3.

The data are:

(1) $[SO^3, Aq] = 39{,}170$: (this is Thomsen's number for *liquid* SO_3).

Then, as $[S, O^3, Aq] - [SO^3, Aq] = [S, O^3]$, it follows from the values already given that

$$[S, O^3] = 103{,}247 \text{ (the } SO_3 \text{ produced being liquid).}$$

(2) When SO_3 dissolves in water a solution of H_2SO_4 is obtained; therefore the reaction $SO_3 + Aq = H_2\ SO_4\ Aq$, is more properly written $SO_3 + H_2O + Aq = H_2SO_4\ Aq$. But we have already obtained the thermal value of this reaction, viz. 39,170 [see (1)]. Moreover the thermal value of the action which occurs when H_2SO_4 dissolves in water has been determined to be 17,850.

We have now these data:

$$[SO^3, H^2O, Aq] = 39{,}170;\ [H^2SO^4, Aq] = 17{,}850;$$

$$\therefore\ [SO^3, H^2O] = 39{,}170 - 17{,}850 = 21{,}320.$$

Finally, to find the thermal value of the reaction

$$H_2 + S + O_4 = H_2SO_4,$$

it is only necessary to add together the values we have deduced for the various parts of this reaction.

These are

$$[S, O^3] = 103{,}247;\ [H^2, O] = 68{,}360;\ [SO^3, H^2O] = 21{,}320;$$

$$\therefore\ [H^2, S, O^4] = 192{,}927 \text{ gram-units.}$$

VI. Required the heat of formation of hydrobromic acid, HBr, from its elements (gaseous hydrogen and liquid bromine).

The heat developed in the reaction $H + Br = HBr$ cannot be determined by direct measurement, but it may be calculated in the following manner.

An aqueous solution of potassium bromide is partly decomposed by gaseous chlorine; the heat evolved is measured; and the quantities of potassium chloride, potassium bromide, and bromine present in solution at the close of the reaction are determined. Data are thus obtained for finding the thermal value of the reaction[1] $KBr\ Aq + Cl = KCl\ Aq + Br$.

Thomsen's result was $[KBr\ Aq, Cl] = 11{,}478$.

But this reaction is composed of two parts: it may be written thus,

$$[KBr\ Aq, Cl] = [K, Cl, Aq] - [K, BrAq].$$

The bromine reacts as a solution of bromine in water throughout the changes to be considered.

Now let us analyse the two reactions expressed in the thermal formulae [K, Cl, Aq] and [K, Br Aq].

An aqueous solution of potassium chloride is produced by neutralising an aqueous solution of hydrochloric acid by an aqueous solution of caustic potash ; thus,

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[1] For details see Thomsen, *loc. cit.* 2. 21.

All correction [illegible]

$$KOHAq + HCl\,Aq = KClAq + H_2OAq.$$

When this reaction is regarded from the thermal point of view it may be thus expressed,

$$[KOHAq, HClAq] = [K, Cl, Aq] + [H^2, O, Aq] - [K, O, H, Aq] - [H, Cl, Aq] ;$$

$$\therefore [K, Cl, Aq] = [KOH\,Aq, HCl\,Aq] + [K, O, H, Aq] + [H, Cl, Aq] - [H^2, O, Aq].$$

Similarly the production of an aqueous solution of potassium bromide may be thus expressed,

$$[KOH\,Aq, HBr\,Aq] = [K, Br\,Aq] + [H^2, O, Aq] - [K, O, H, Aq] - [H, Br\,Aq] ;$$

$$\therefore [K, Br\,Aq] = [KOH\,Aq, HBr\,Aq] + [K, O, H, Aq] + [H, Br\,Aq] - [H^2, O, Aq].$$

From this it follows that

$$[K, Cl, Aq] - [K, Br\,Aq] = [KOH\,Aq, HClAq] - [KOH\,Aq, HBr\,Aq] + [H, Cl, Aq] - [H, Br\,Aq].$$

The thermal value of this change, as we have seen, is 11,478 gram-units. But Thomsen has also determined the values of three out of the four parts of which the total change consists; his results are represented thus,

$$[H, Cl, Aq] = 39{,}315 ;\ [KOH\,Aq, HCl\,Aq] = 13{,}740 ;\ [KOH\,Aq, HBr\,Aq] = 13{,}740.$$

Therefore it follows that

$$[H, Br\,Aq] = 39{,}315 + 13{,}740 - 13{,}740 - 11{,}478,$$
$$= 27{,}837 \text{ gram-units.}$$

Moreover the heat of solution of bromine in water has been determined :—

$$[Br, Aq] = 539.$$

But

$$[H, Br, Aq] = [Br, Aq] + [H, Br\,Aq],$$
$$= 539 + 27{,}837,$$
$$= 28{,}376.$$

It only remains now to find the heat of solution in water of hydrobromic acid :—

$$[HBr, Aq] = 19{,}936.$$

$$\begin{aligned} \text{But}\quad [\mathrm{H, Br}] &= [\mathrm{H, Br, Aq}] - [\mathrm{HBr, Aq}], \\ &= 28{,}376 - 19{,}936, \\ &= 8{,}440. \end{aligned}$$

That is, the heat of formation of gaseous HBr from its elements = 8,440 gram-units.

61. The examples given in the preceding paragraph suffice to illustrate the methods whereby the thermal value of a definite chemical change is calculated when the value cannot itself be directly determined. The underlying principle is always one, viz. the total change of energy accompanying the change of a chemical system from one definite state to another is independent of the intermediate states through which the system may pass. Assuming that the total energy-change is represented by the quantity of heat evolved or absorbed, it follows that the total thermal change during a chemical operation is dependent only on the initial and final states of the chemical system.

In applying this principle we have sometimes started with a system in a certain configuration (call this A); we have measured the thermal change accompanying the passage to another configuration (call this C); we have then started with the same elementary constituents but differently arranged (call this configuration B), and measured the thermal change accompanying the passage to the same final configuration (C) as before. We have then concluded that the difference between these two thermal changes represents the thermal value of the change of the system from configuration A to configuration B.

In other cases we have had to deal with a chemical reaction which could be resolved into parts, the thermal values of some of which, but not of all, could be directly determined. In such cases we have measured the thermal value of the total change, and by deducting from this the thermal value of a particular part, or the sum of the values of particular parts, determined by separate experiments, we have been able to find the thermal value of that part of the total change which could not be found by direct experiment.

In separating a chemical operation into parts each of which is to be examined thermally, it is important that these partial changes should be as simple as possible. It is also important that they should not involve any marked physical changes, otherwise the thermal value of a partial change may itself be the sum of so many reactions that no trustworthy conclusions can be drawn regarding the quantity of heat produced or absorbed during the primary chemical reaction which we wish to study.

For data regarding heats of combustion and formation of compounds see Appendix I.

CHAPTER III.

APPLICATIONS OF THERMAL METHODS TO THE STUDY OF CHEMICAL PHENOMENA.

SECTION I. *Allotropy and Isomerism.*

62. IF chemical composition is one of the variables on which the state of a specified material system depends, and if the energy of the given system is conditioned by the state of that system (see *ante*, Chap. I. par. 16), then there must be definite quantitative connections between changes of energy and those changes of chemical composition which are connoted by the terms *allotropy* and *isomerism.*

63. Two distinct forms of the element phosphorus are known. In other words, two kinds of matter are known, each characterised by its own properties (e.g. melting point, crystalline form, solubility in a given liquid &c.) and yet each wholly transformable into the other without loss or gain of mass, and each yielding the same mass of the same new kind of matter under similar conditions (e.g. 1 gram of either phosphorus when burnt produces 2·29 grams of phosphorus pentoxide). Phosphorus, sulphur, carbon, silicon, boron, oxygen and some other elements exist in more than one form; they exhibit the phenomenon of allotropy. The change of yellow into red phosphorus, that of oxygen into ozone, that of prismatic into octahedral sulphur, &c. are allotropic changes.

64. Many compounds, especially carbon compounds, are known all having the same percentage composition and the same density in the gaseous state, and yet each differing more

or less from the others both in chemical and physical properties. Thus the composition and the density as gases of ethylic alcohol and methylic oxide are expressed by the formula C_2H_6O; but these compounds differ considerably in their properties. There are three dibromobenzenes, $C_6H_4Br_2$, each characterised by a definite boiling-point &c., and by its behaviour towards such reagents as caustic potash or nitric acid. Alcohol and methylic oxide on the one hand, and the three dibromobenzenes on the other hand are said to exhibit isomerism: the change from alcohol to methylic oxide, or from one dibromobenzene to another, is called an isomeric change[1].

65. The phenomena of allotropy and isomerism are included in the conception of chemical composition. The molecular theory asserts that the properties of any specified kind of matter are the properties of the molecules of which that matter is built up; and that the properties of these molecules are conditioned by the nature, number, and relative arrangement of the parts of the molecules, that is, of the atoms which compose the molecules. Experiment has shewn that the molecule of oxygen is diatomic while that of ozone is triatomic. In this case we have certain properties associated with the existence of molecules each composed of two atoms of the same kind, viz. oxygen, and we have other properties associated with the existence of molecules each composed of three atoms of the same kind of matter, which kind of matter is again oxygen. It is possible that each kind of phosphorus, or sulphur, or carbon &c. has a different molecular weight from each other kind, but we have as yet no direct experimental evidence in support of this view. The whole of the modern so-called constitutional or structural formulæ are based on the assumption that the properties of a molecule are conditioned not only by the nature and number, but also by the relative arrangement of the atoms in that molecule. We attempt, in a crude way, to represent such relative arrangements in our formulæ, making use of certain subsidiary assumptions and conventions. Thus we write the formula of alcohol as $C_2H_5.OH$, and that of methylic oxide as $H_3C.O.CH_3$ and we assume (among other

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[1] The student should carefully study the phenomena of allotropy and isomerism from the chemical point of view.

things) that in the former molecule there is direct mutual action between one of the carbon atoms and the oxygen atom, whereas in the second molecule there is direct mutual action between the oxygen atom and each of the atoms of carbon.

66. The known thermal data regarding allotropic changes are not very numerous: the following numbers shew that there is a definite quantitative connection between these changes and the running down of energy to the form of heat.

$[P^2, O^5] = 369{,}100$ gram-units, where P_2 is 62 grams of ordinary phosphorus (P_α);

$[P^2, O^5] = 326{,}800$ gram-units, where P_2 is 62 grams of amorphous phosphorus (P_β).

Hence the change of 31 grams of ordinary phosphorus into the same mass of amorphous phosphorus is attended with the evolution of 21,150 units of heat.

$[2Oz = 3O^2] = 59{,}200$. That is, the change of 96 grams of ozone into 96 grams of oxygen is attended with the evolution of 59,200 units of heat.

67. A considerable mass of data regarding the thermal values of isomeric changes has been accumulated. The following numbers serve to illustrate the connection between this class of chemical reactions and the running down of energy[1].

Heats of combustion of isomeric compounds.

C_6H_6.

I. Benzene = 788,000. II. Dipropargyl = 883,200.

C_3H_6O.

I. Acetone = 424,000. II. Propaldehyde = 426,000.
III. Allylalcohol = 443,000.

$C_3H_6O_2$.

I. Ethylic formate = 390,000. II. Methylic acetate = 395,000.

$C_2H_4O_2$.

I. Acetic acid = 210,000. II. Methylic formate = 252,000.

C_2H_6O.

I. Ethylic alcohol = 330,000. II. Methylic oxide = 344,000.

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[1] For further data, see Appendix II.

$C_6H_4(OH)CO_2H$.

I. Parahydroxybenzoic acid = 752,000. II. Meta-acid = 754,000.
III. Ortho-acid = 759,000.

68. The data on this subject are not sufficient to warrant any but the broadest generalisations. It is probable that the differences between the energies of isomeric molecules largely depend on these three conditions:—

(1) Whether each atom in the molecule acts on, and is acted on by, the maximum number of other atoms; in other words whether each atom exhibits its maximum valency in the given molecule.

(2) On the nature of the atoms between which direct mutual action occurs within the molecule.

(3) On the symmetry of the structure of the molecules.

If the structural formulæ of the compounds in the foregoing table are compared it will be seen: (i) that dipropargyl, which is a compound belonging to the paraffinoid group of carbon compounds, contains more energy than the isomeric molecule benzene, which belongs to the benzenoid group of carbon compounds; (ii) that of the three isomeric hydroxybenzoic acids, all of which are benzenoid compounds, the para-compound, which is the most symmetrical, contains the least, and the ortho-compound the most energy; and (iii) that of two or more isomeric paraffinoid molecules, that containing the greatest number of tetravalent carbon atoms contains the smallest quantity of energy, provided the distribution of the atomic interactions is the same, or nearly the same, in the molecules. But these three conclusions are only special cases coming under the broad generalisations already stated.

69. There is a great difficulty attending the chemical interpretation of such thermal data as we are now considering. When we make such statements as the three generalisations in par. 68 we use language which may have a precise meaning, but which is not unfrequently employed without any meaning at all. Now unless the language in which we express the chemical aspect of the twofold change (change of energy and change of material configuration) means something, the supposed

explanation is no explanation, but is only a form of words 'full of sound...signifying nothing.' Such expressions as 'tetravalent atoms,' 'distribution of atomic interactions,' 'para-, ortho-, meta-compounds,' 'paraffinoid and benzenoid compounds,' 'symmetrical and unsymmetrical molecules,' must be used as summarising facts in the language of a special theory; they must call up in the mind of the student more or less clear-cut mental images, else they have no scientific value, or rather their value is a negative quantity. But to explain these terms would be out of place here. I am assuming in the reader of this book some knowledge of chemical principles. It is of the utmost importance that before going further he should have clear conceptions regarding the methods of obtaining structural formulæ, and the facts which these formulæ summarise and suggest. In what follows I shall assume the existence of such conceptions. I shall employ structural formulæ, where necessary, and shall use such expressions as 'monovalent' or 'polyvalent atoms,' 'maximum valency of an atom in a specified molecule,' 'distribution of atomic interactions,' and the like, in the sense, and with the meaning, given to these formulæ and these expressions by Lossen[1].

70. Now I think it is evident that could we connect definite changes of energy with definite isomeric changes we should have done a good deal towards measuring one class of relations between composition and properties. We must, it is true, express the changes of configuration which we study in isomerism in terms of a special theory of the structure of matter, and the terms employed are not so expressive as at first sight they seem to be. But great advances in the study of chemical composition have been made by applying the molecular theory to the phenomena of isomerism. If only we can keep within the definitions of the theory, and if, when a difficulty occurs, we can refrain from introducing a new hypothesis without acknowledging it to ourselves or to others, then, I think, the thermal study of isomeric changes must advance the science of chemistry, even if that science is forced to content itself with

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[1] Lossen's views are stated and discussed in detail in my *Principles of Chemistry*, Book I. Chap. II.

such partial conceptions of the mechanism of these changes as it now possesses. We have plenty of data regarding isomerism from the purely chemical standpoint; what we now require is measurements of the energy-changes which accompany these material changes. We do not, I think, want to add indefinitely to the list of compounds to each of which a constitutional formula is given; we rather want to know more about the compounds already prepared. We want to classify these compounds, so that we may see connections between transformations of energy and transformations of matter, because by doing this we hope to rise from empirical statements to general principles.

71. The only serious attempt which has yet been made to trace definite connections between changes of molecular structure and changes of energy has not, it appears to me, been very successful. But I believe the failure is to be traced to the dominating influence of certain idols of the market place. The tyranny of phrases has here, as so often before, led the investigator captive.

72. Thomsen[1] has endeavoured to measure what he calls the 'dynamic value of each of the bonds of carbon.'

It is almost impossible to attach any precise meaning to the expression 'a bond,' as this is used in the various text books, and by different chemists.

The atom of hydrogen is monovalent, that is, an atom of hydrogen, so far as we know, never directly acts on and is acted on by more than a single other atom in a molecule. The atom of oxygen is divalent, that is, an atom of oxygen can directly act on and be acted on by two other atoms in a molecule: but in some molecules, e.g. in the molecule CO, there are only two atoms, one of which is oxygen.

The theory of bonds uses a language of its own to express the foregoing statements. It speaks of the hydrogen atom as having one bond, and the atom of oxygen as having two bonds: when two atoms of hydrogen combine with one of oxygen to form a molecule of water-gas, the theory says that each bond of the oxygen atom is satisfied by the bond of a hydrogen atom; when the molecule CO is formed, it says that both oxygen bonds are satisfied by two bonds of the carbon atom. But the atom of carbon is tetravalent. What then becomes of the two remaining bonds of the carbon atom in the molecule CO? They satisfy one another, says the bond-theory; or they remain free and unsatisfied, say some chemists who on the whole support the theory of bonds.

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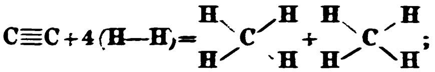
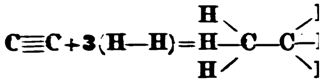
[1] *Ber.* **13.** 1321; and *Journal für prakt. Chem.* (2) **23.** 157 and 163.

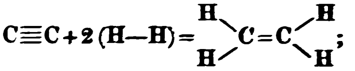
73. Consider these four transactions:—

$$(1)\ C_2+H_8=2CH_4;\quad (2)\ C_2+H_6=C_2H_6;\quad (3)\ C_2+H_4=C_2H_4;$$
$$(4)\ C_2+H_2=C_2H_2.$$

Each operation represents the formation of a hydrocarbon molecule (or molecules). The bond-theory represents these transactions in this way,

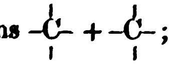
(1) 

(2) 

(3) 

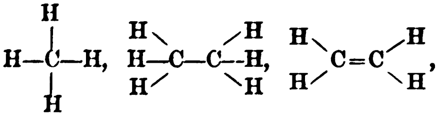
(4) $C\equiv C+H-H=H-C\equiv C-H;$

Each reaction consists (by the theory) of various parts:—

(*a*) Separation of the diatomic molecule $C\equiv C$ into the atoms 

(*β*) Separation of two or more diatomic molecules $H-H$ into the atoms $H-$, $H-$;

(*γ*) Combination of these atoms to form the new molecules



or $H-C\equiv C-H$.

Now (*a*) and (*β*) occur in all the reactions under consideration, but (*γ*) varies in each of these reactions. In the formation of the molecule CH_4 we have, says the bond-theory, a combination of one atom of carbon with four atoms of hydrogen to form a molecule wherein each carbon bond is satisfied by a hydrogen bond; but in the three other reactions we have molecules produced wherein one carbon bond is satisfied by another carbon bond (C_2H_6), or two carbon bonds are satisfied by two carbon bonds (C_2H_4), or lastly three carbon bonds are satisfied by three carbon bonds (C_2H_2). Hence if the total thermal value of each reaction can be determined, and if the thermal values of the parts we have called (α) and (β) can be determined, we shall have data for calculating the thermal value of the part we have called (γ).

To determine the total thermal value of each of the four reactions is to determine the heat of formation of CH_4, C_2H_6, C_2H_4, and C_2H_2 respectively. We have already learned the principle by which this can be done[1].

In order that atoms of carbon, represented by the bond-theory as $-\overset{|}{\underset{|}{C}}-$, $-\overset{|}{\underset{|}{C}}-$ &c., should be produced from solid carbon, the carbon must be gasified; that is, heat must be added until a mass of molecules $C \equiv C$ is obtained, and then more heat must be added until these molecules are separated into atoms $-\overset{|}{\underset{|}{C}}-$, $-\overset{|}{\underset{|}{C}}-$ &c.

Now consider the two reactions $C + O = CO$, and $C + O_2 = CO_2$. Starting with solid carbon, the first of these reactions may be represented thermally as consisting of two parts; (1) absorption of heat in order to gasify one atom of carbon, and (2) evolution of heat by the combination of this atom with an atom of oxygen. Similarly the second reaction may be regarded from a thermal point of view as consisting of two parts; (1) absorption of heat in order to gasify one atom of carbon, and (2) evolution of heat by combination of this atom with two atoms of oxygen. Let the thermal value of (1) be represented by $-d$, and that of (2), when CO is produced, by k. Let us now set down the actual thermal values experimentally determined; we have

$$[C, O] = 29{,}290 = -d + k$$
$$[C, O^2] = 96{,}960 = -d + 2k,$$

assuming, that is to say, that the thermal value of the addition of each oxygen atom to a gaseous carbon atom to form the molecule CO_2 is the same[2].

From these equations it follows that

$$k = 67{,}670$$
$$d = 38{,}380.$$

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[1] See *ante*, Chap. I. pars. 58—60.

[2] Thomsen deduces experimental evidence in favour of this assumption; see his *Untersuchungen*, 2. 106—109. See also Mendelejeff, Ber. 15. 1555; or *C. S. Journal* **Abstracts** for 1882, 916.

Now if we use the symbol r to represent the thermal value of the combination of an atom of hydrogen with an atom of gaseous carbon, and if we assume that this value is always constant in all hydrocarbons whether the atom of carbon has or has not already combined with hydrogen atoms, we get, according to Thomsen, the following equations, expressing the heats of formation (for constant volume) of various hydrocarbons :—

$$\begin{aligned}
&(1)\quad [C, H^4] = 21{,}170 = -d + 4r\\
&(2)\quad [C^2, H^6] = 27{,}400 = -2d + 6r + v_1\\
&(3)\quad [C^2, H^4] = -3{,}290 = -2d + 4r + v_2\\
&(4)\quad [C^2, H^2] = -48{,}170 = -2d + 2r + v_3.
\end{aligned}$$

The symbol v_1 here represents the thermal value of the 'single linking' of two gaseous carbon atoms, or the combination of these two atoms by one bond of each; v_2 represents the thermal value of the combination of a pair of gaseous carbon atoms by two bonds, and v_3 the combination of a pair of gaseous carbon atoms by three bonds.

Now let us see how Thomsen proposes to find the values of r and v_1 &c.

The following numbers are obtained from experimental results :—

$$\begin{aligned}
&(a)\quad C_2H_6 + H_2 = 2CH_4 = 14{,}940 \text{ thermal units.}\\
&(b)\quad C_2H_4 + 2H_2 = 2CH_4 = 45{,}630 \quad ,, \qquad ,,\\
&(c)\quad C_2H_2 + 3H_2 = 2CH_4 = 90{,}510 \quad ,, \qquad ,,
\end{aligned}$$

In (*a*) we have (i) separation of the 'single linking' of two carbon atoms in the molecule C_2H_6, and (ii) combination of two atoms of hydrogen with the residues CH_3;

$$\text{hence, } 2r - v_1 = 14{,}940. \quad (1)$$

In (*b*) we have (i) separation of the 'double linking' of two carbon atoms in the molecule C_2H_4, and (ii) combination of four atoms of hydrogen with the residues CH_2;

$$\text{hence, } 4r - v_2 = 45{,}630. \quad (2)$$

In (*c*) we have (i) separation of the 'treble linking' of two carbon atoms in the molecule C_2H_2, and (ii) combination of six atoms of hydrogen with the residues CH;

$$\text{hence, } 6r - v_3 = 90{,}510. \quad (3)$$

From equations (1) (2) and (3) r may be eliminated, and *the following relations* may be found :—

$$\left.\begin{array}{l}2v_1 - v_2 = 15{,}750\\3v_1 - v_3 = 45{,}690\end{array}\right\} \quad (4)$$

Then turning back to the four equations already given on p. 70 as representing the heats of formation of CH_4, C_2H_6, C_2H_4, and C_2H_2, we can determine the value of r from equation (1), and the values of v_1, v_2, and v_3 from equations (2) (3) and (4).

The values thus obtained are these :—

$$r = 14{,}887\,;\; v_1 = 14{,}835\,;\; v_2 = 13{,}920\,;\; v_3 = -1{,}185.$$

The following are the general conclusions which Thomsen draws from this investigation[1].

(1) Much heat is absorbed in the process of changing solid into gaseous carbon, viz. 38,380 gram-units for each atom of carbon.

(2) When one atom of hydrogen combines with one atom of gaseous carbon 14,830 gram-units of heat are evolved.

(3) The combination of two gaseous carbon atoms is attended with the evolution of much heat, provided these atoms combine by one, or two bonds.

(4) When two gaseous carbon atoms combine by three bonds no heat is evolved; a little heat is indeed absorbed.

74. The fundamental assumption made by Thomsen in this investigation is that the molecule of gaseous carbon is diatomic. The only apparent reason for making this assumption is that it becomes easy to speak of two carbon atoms as united by one, two, three, or four bonds in the molecule C_2. On p. 17 are given the data on which the classification of elementary molecules in accordance with their atomicity must be based. If the student considers the table there given he will be convinced that Thomsen's assumption of the diatomicity of the carbon molecule is quite unjustified. Some of the results which Thomsen has himself arrived at appear to oppose this assumption. Thus, how is it possible that two free gaseous atoms can combine together with absorption of heat unless the process of combination is complex, and consists of two parts, (1) separation of the atoms into parts with absorption of much heat, and (2) combination of these parts with evolution of less heat than was absorbed in (1)? Again the fact that the specific heat of carbon increases very considerably with increase of temperature suggests that the

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[1] *Untersuchungen*, 2. 112.

molecule of carbon, or at least the reacting unit of solid carbon, is a complex structure.

75. If one carefully examines Thomsen's conclusions one will, I think, find that they are meaningless; or that they completely demolish the theory of bonds which they are supposed to support.

A bond is a 'unit of affinity', or a 'unit of atom-fixing power;' at any rate it is always spoken of as a unit of some kind. Now when one 'bond' of a carbon atom is 'satisfied' by one bond of another carbon atom, there is, according to Thomsen, a running down of energy which is measured by the evolution of about 15,000 gram-units of heat; when two bonds of a carbon atom are satisfied by two bonds of another carbon atom, there is a running down of energy which is measured by the evolution of about 14,000 gram-units of heat; and when three bonds of a carbon atom are satisfied by three bonds of another carbon atom, there is a gain of energy which is measured by the absorption of about 1200 gram-units of heat. Compare this unit, the 'bond,' with another unit in common use. One would be slightly surprised to discover that two feet were equal to one, and that three feet when added together measured a little less than nothing. Moreover the value of this 'unit of atom-fixing power' varies according to the nature of the atom fixed. The dynamical value (to use Thomsen's expression) of a carbon bond is variable; it differs according as the atom combines with carbon or with hydrogen atoms.

The truth seems to be that the conception which underlies the word 'bond' is not a dynamical conception, although the language used by the upholders of the hypothesis is for the most part based on and derived from dynamical notions.

It must surely be a legitimate object of research to determine the 'numerical values of the dynamical constants of carbon', that is, according to Thomsen, the constants on which the thermal values of the formation and decomposition of carbon compounds depend; but among those constants we cannot, I think, place the value of the 'bond'.

The notion of the bond was unfortunately introduced to help chemists to clearer views regarding the valencies of atoms *in molecules.* At first chemists used the bond as an illustration;

they introduced it with an apologetic 'as it were'; but before long they forgot that there were facts underlying the words used; the words became everything, and as usual the tyranny of phrases has proved unbearable.

76. Many difficulties attend all attempts to apply thermal methods to the study of isomeric changes. We have as yet no kinetic theory of solids and liquids, and the only feasible theory of the mechanism of chemical change is strictly applicable to gases alone. If thermal data bearing on the subject of isomerism are accumulated I think we shall have to attempt a classification of isomerides for the most part independently of the prevalent chemical views regarding the structure of molecules. Shall we place the stable isomerides in one class, and the unstable isomerides in another, stability being measured by the greater or less loss of energy attending the formation of the different isomerides from the same materials? But in most cases part of the energy lost will be the accompaniment not of chemical but of physical changes. How shall we separate these two kinds of change? Unless this separation can be made we may arrive at very wrong conclusions regarding the stability of isomerides: an isomeride which from purely thermal data is classed as chemically stable, may turn out to be chemically unstable; the large heat-evolution attending the formation of the compound may be due to subsidiary physical occurrences which accompany the primary chemical change.

For data regarding heats of combustion of isomerides see Appendix II.

SECTION II. *Neutralisation of acids by bases, and of bases by acids.*

77. The study of the phenomena of neutralisation is one well suited for the application of thermal methods. The chemical changes to be considered occur between compounds in dilute aqueous solutions, and the influence of subsidiary physical changes is thus reduced to a mimimum[1]. The subject of study

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[1] See *post*, par. 199.

is also always a chemical operation, rather than an individual compound; and operations, or processes of change, form the proper subject-matter of chemistry.

The first volume of Thomsen's *Thermochemische Untersuchungen* is devoted to a consideration of the neutralisation of acids and bases.

78. *The heat of neutralisation*, of an acid by a base or of a base by an acid, is defined as the number of gram-units of heat evolved when equivalent[1] quantities, in grams, of the acid and base are mixed in dilute aqueous solutions, the products of the action being also soluble in water.

Thomsen employs a solution of 2NaOH (grams) in about 400 H_2O (grams) as the standard base, and a solution of H_2SO_4 (grams) in about 400 H_2O (grams) as the standard acid.

The thermal values of the following reactions represent the heats of neutralisation of various acids and bases.

$[2\mathrm{NaOHAq}, 2\mathrm{H}X\mathrm{Aq}]$ in the case of a monobasic acid
$[2\mathrm{NaOHAq}, \mathrm{H}^2X\mathrm{Aq}]$,, dibasic ,,
$[2\mathrm{NaOHAq}, \frac{2}{3}\mathrm{H}^3X\mathrm{Aq}]$,, tribasic ,,
$[2\mathrm{NaOHAq}, \frac{1}{2}\mathrm{H}^4X\mathrm{Aq}]$,, tetrabasic ,,
(X = acid radicle);

$[\mathrm{H}^2\mathrm{SO}^4\mathrm{Aq}, 2\mathrm{MOHAq}$ or $2\mathrm{N}X^3\mathrm{Aq}]$ in the case of a monacid base
$[\mathrm{H}^2\mathrm{SO}^4\mathrm{Aq}, \mathrm{M(OH)}^2\mathrm{Aq}$ or $\mathrm{N}^2X^6\mathrm{Aq}]$,, diacid ,,
$[\mathrm{H}^2\mathrm{SO}^4\mathrm{Aq}, \frac{2}{3}\mathrm{M(OH)}^3\mathrm{Aq}$ or $\frac{2}{3}\mathrm{N}^3X^9\mathrm{Aq}]$,, triacid ,,
$[\mathrm{H}^2\mathrm{SO}^4\mathrm{Aq}, \frac{1}{2}\mathrm{M(OH)}^4\mathrm{Aq}$ or $\frac{1}{2}\mathrm{N}^4X^{12}\mathrm{Aq}]$,, tetracid ,,
(X = H, or a radicle C_nH_{2n+1}).

79. Thomsen divides the commoner acids into four groups according to the values of their heats of neutralisation.

I. Those acids which have a heat of neutralisation approximately equal to 20,000 gram-units:—

HNO_2, HClO, $H_2B_2O_4$, H_2CO_3 &c.

II. Those acids which have a heat of neutralisation approximately equal to 25,000 gram-units:—

H_2CrO_4, $C_2H_4(CO_2H)_2$, $CH_2CHOH(CO_2H)_2$ &c.

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[1] The student should note here that *equivalent*, not molecular, quantities of acids and bases are employed: e.g. $Na_2O_2H_2$ and H_2SO_4 and $H_2N_2O_6$ express equivalent quantities of soda, sulphuric acid, and nitric acid respectively.

III. Acids with a heat of neutralisation nearly equal to 27,000 gram-units:—

HCl, HBr, HI, $HClO_3$, $HBrO_3$, HIO_3, HNO_3, $H_2S_2O_3$,
H_2SiF_6, HCO_2H, CH_3CO_2H &c.

Most of the acids examined by Thomsen belong to this group.

IV. Acids having a heat of neutralisation greater than 27,000 units, and varying from 28,000 to 32,500 units:—

$CH_2Cl.CO_2H$, $CHCl_2.CO_2H$, $CCl_3.CO_2H$, $H_2C_2O_4$, H_3PO_2,
H_2SO_3, H_2SO_4, H_2SeO_4, HF, HPO_3 &c.

The heat of neutralisation of a few acids is less than 20,000 units.

80. The bases which are soluble in water may be divided into two groups, so far as their heats of neutralisation are concerned.

I. The group of the hydroxides, represented by NaOH and KOH. The mean value of the heat of neutralisation of bases in this group is 31,350 gram-units. The group comprises the following bases:—

$LiOH$, $NaOH$, KOH, $TlOH$; $Ca(OH)_2$, $Sr(OH)_2$,
$Ba(OH)_2$[1]; $N(CH_3)_4OH$, $(C_2H_5)_3SOH$, $Pt(NH_3)_4(OH)_2$.

II. The group of the anhydrous bases, or the amines, represented by NH_3. The mean value of the heat of neutralisation of bases in this group is 28,000 gram-units. The group comprises NH_3 and the amines $NH_2(C_nH_{2n+1})$ and $NH(C_nH_{2n+1})_2$. The substitution of negative radicles for H in the molecule NH_3 is attended with a considerable decrease in the heat of neutralisation of the base; thus

$$[2NH^2(C^6H^5)Aq,\ H^2SO^4Aq] = 15{,}500,$$
and $$[2NH^2(C^7H^7)Aq,\ H^2SO^4Aq] = 15{,}200;$$
also $$[2NH^2OH\quad Aq,\ H^2SO^4Aq] = 21{,}600.$$

When CO is substituted for H_2 in $2NH_3$ the heat of neutralisation of the product $[(NH_2)_2CO]$ is almost equal to nothing.

81. The basicity of an acid the formula of which is known may be determined by measuring the quantity of heat evolved

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[1] See *post*, pars. 96, 97.

during the reaction of one formula-weight[1] of the acid, in dilute aqueous solution, on $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, 1, 2 &c. formula-weights of soda, also in dilute aqueous solution. Thus consider the following thermal values :—

Action of HCl Aq on NaOH Aq.

$[HClAq, \frac{1}{2}NaOHAq]$ = about 6,000
$[HClAq, NaOHAq]$ = ,, 13,500
$[HClAq, 2NaOHAq]$ = ,, 13,500.

Action of H_2SO_4 Aq on NaOH Aq.

$[H^2SO^4Aq, \frac{1}{2}NaOHAq]$ = about 7,000
$[H^2SO^4Aq, NaOHAq]$ = ,, 14,500
$[H^2SO^4Aq, 2NaOHAq]$ = ,, 31,000
$[H^2SO^4Aq, 3NaOHAq]$ = ,, 31,000.

Action of $C_6H_8O_7$ Aq on NaOH Aq.

$[C^6H^8O^7Aq, NaOHAq] = 12{,}400$
$[C^6H^8O^7Aq, 2NaOHAq] = 24{,}800$
$[C^6H^8O^7Aq, 3NaOHAq] = 38{,}000$
$[C^6H^8O^7Aq, 4NaOHAq] = 38{,}000.$

From these data we conclude that hydrochloric acid is a monobasic, sulphuric acid a dibasic, and citric acid a tribasic acid.

When one formula-weight of soda and one of hydrochloric acid react, as much heat is evolved as when twice, or more than twice this quantity of soda is used; but the action of two formula-weights of soda on one of sulphuric acid evolves, in round numbers, twice as much heat as the action of half this quantity of soda; in the case of citric acid it is necessary to add three formula-weights of soda to one of acid before the maximum evolution of heat is attained.

82. The quantity of heat evolved during the neutralisation of a dibasic acid is sometimes divisible into two exactly equal parts, according as one or two formula-weights of soda are allowed to react with one formula-weight of the acid. In other cases the thermal value of each stage of the total operation is different. Thus consider the following data[2] :—

$[H^2SiF^6Aq, NaOHAq] = 13{,}300$
$[H^2SiF^6Aq, 2NaOHAq] = 2 \times 13{,}300.$

$[H^2SO^4Aq, NaOHAq] = 14{,}750$
$[H^2SO^4Aq, 2NaOHAq] = (2 . 14{,}750) + 1{,}900.$

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[1] The formulæ HCl, H_2SO_4, H_3PO_4, $H_2C_2O_4$ &c. do not represent equivalent quantities of the acids formulated; nor do they represent, in all cases, molecular weights. The term formula-weight is cumbrous, but I think it expresses a definite quantity of the substance under consideration.

[2] Thomsen, *loc. cit.*, **1**. 302—6.

$$[H^2SO^3Aq, \quad NaOHAq] = 15{,}850$$
$$[H^2SO^3Aq, 2NaOHAq] = (2 . 15{,}850) - 2{,}750.$$

83. Each of these three acids represents a group. Thomsen divides the dibasic acids examined by him into three groups, according as the thermal value of the action of the second formula-weight of soda is (1) equal to, (2) greater than, or (3) smaller than, the value of the action of the first formula-weight[1]. The data are presented in the following table :—

Group I.

Heat evolved in action of NaOH	Acid	
	H_2SiF_6	H_2PtCl_6[2]
1st formula-weight	13,300	13,600
2nd ,, ,,	13,300	13,600.

Group II.

	H_2SO_4	H_2SeO_4	$H_2C_2O_4$	$H_2C_4H_4O_6$
1st ,, ,,	14,750	14,750	13,850	12,450
2nd ,, ,,	16,650	15,650	14,450	12,850.

Group III.

	H_2SO_3	H_2SeO_3	H_2CO_3	$H_2B_2O_4$
1st ,, ,,	15,850	14,750	11,000	11,100
2nd ,, ,,	13,100	12,250	9,150	8,900
	H_2CrO_4	H_2PHO_3	$C_2H_4(CO_2H)_2$	
1st ,, ,,	13,150	14,850	12,400	
2nd ,, ,,	11,550	13,600	11,750.	

84. The tribasic acids examined by Thomsen may also be classified according as the thermal value of the action of the second formula-weight of soda is greater or smaller than that of the first, and the value of the action of the third formula-weight is greater or smaller than that of the second. The data are as follows :—

Group I.

Heat evolved in action of NaOH	Acid	
	$H_3C_6H_3O_6$ (Aconitic Acid)	$H_3C_6H_5O_7$ (Citric Acid)
1st formula-weight	12,850	12,650
2nd ,, ,,	12,950	12,800
3rd ,, ,,	13,350	13,550.

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[1] Thomsen, *loc. cit.*

[2] But see Thomsen, *loc. cit.*, **1.** 229: it is doubtful whether the numbers given really represent the thermal value of the action of soda on this acid.

GROUP II.

Heat evolved in action of NaOH	Acid H_3AsO_4	Acid H_3PO_4
1st formula-weight	15,000	14,850
2nd „ „	12,600	12,250
3rd „ „	8,350	6,950.

Group I. of the tribasic acids corresponds to Group II. of the dibasic, and Group II. of the tribasic to Group III. of the dibasic acids.

85. Thomsen suggests that this classification of dibasic and tribasic acids may be summarised in the following typical formulæ:—

Dibasic Acids.

Acid of Group I.	Typical formula	RH_2	e.g. $SiF_6 . H_2$;
„ II.	„	$R(OH)_2$	e.g. $SO_2(OH)_2$;
„ III.	„	$R(OH)H$	e.g. $SO_2(OH)H$.

Tribasic Acids.

Acid of Group I.	Typical formula	$R(OH)_3$	e.g. $C_6H_5O_4(OH)_3$;
„ II.	„	$HR(OH)H$	e.g. $HPO_3(OH)H$.

Let us now consider Thomsen's results and conclusions in a little more detail[1].

86. As regards monobasic acids: the addition of more soda than suffices to produce the normal salt of one of these acids, or the addition of the acid itself to the normal sodium salt, is attended by practically no thermal change, or at most by a thermal change the value of which does not amount to 2 per cent. of the total heat of neutralisation.

87. As regards dibasic acids: we have seen that in the case of every acid, except two, examined by Thomsen, the thermal value of the action of the first quantity of soda added is different from that of the second, equal, quantity of soda. The first of the typical formulæ suggested by Thomsen for the three classes of dibasic acids (par. 85) is probably to be assigned to H_2PtCl_6 and H_2SiF_6 only.

Why should the formula $R(OH)_2$ rather than $R(OH)H$ be assigned to the acids of Group II.? The formula R(OH)H would indicate the easy separation of the acids into anhydride (R) and water (OHH). But the acids placed in Group III. are, as a class, more easily separated into anhydride and water than those placed in Group II. If the differences between the thermal values of the first and second quantities of soda acting on the acids of Group III. are tabulated we have this result:—

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[1] *Loc. cit.*, **1.** 300, *et seq.*

$H_2SO_3 = 2{,}750$; $H_2SeO_3 = 2{,}500$; $H_2CO_3 = 1{,}850$; $H_2B_2O_4 = 2{,}200$; $H_2CrO_4 = 1{,}600$; $H_2PHO_3 = 1{,}250$; $C_2H_4(CO_2H)_2 = 650$.

These differences vary from 9·5 (H_2SO_3) to 2·7 [$C_2H_4(CO_2H)_2$] per cent. of the total heat of neutralisation. We have good evidence in support of the statement that succinic acid is a dihydroxyl compound; therefore, although it occurs in Thomsen's third group, we must place it with those acids the typical formula of which is $R(OH)_2$ i.e. with the acids of Group II. It is fairly easy to separate the other acids of Group III. into anhydride and water.

The formula $CO_2(OH)H$ for carbonic acid is to some extent confirmed by the fact that the higher homologues of this acid although dihydric are distinctly monobasic.

If the differences between the thermal values of the first and second quantities of soda acting on the acids of Group II. are tabulated we have this result:—

$H_2SO_4 = 1{,}900$; $H_2SeO_4 = 900$; $H_2C_2O_4 = 600$; $H_2H_4C_4O_6 = 400$.

These differences vary from 6 (H_2SO_4) to 1·5 ($H_2H_4C_4O_6$) per cent. of the total heat of neutralisation. The differences in the case of acids of Group III. are considerably larger than these. When the difference between the thermal values under consideration is small, and, as a rule, the value of the second quantity of soda is greater than that of the first, Thomsen regards the acid as, generally speaking, belonging to the type $R(OH)_2$; when the difference in question is large, and the value of the second quantity of soda is, as a rule, smaller than that of the first, the acid is regarded as belonging to the type R(OH)H.

88. The behaviour of arsenious acid, or rather of an aqueous solution of the compound As_2O_3, towards soda is peculiar. The oxide As_2O_3 dissolves in water with absorption

of heat: $[As^2O^3, Aq] = -7{,}550$. When soda is added to this solution heat is evolved, and the salt Na_2HAsO_3 is produced. The thermal data are these:—

$$[As^2O^3Aq,\ x\ NaOHAq]$$

$$\begin{array}{ll} x = 1 = \ \ 7{,}300 & \\ & \text{diff.} = 6{,}500 \\ x = 2 = 13{,}800 & \\ & \ \ '' \ \ = 1{,}200 \\ x = 3 = 15{,}000 & \\ & \ \ '' \ \ = \ \ 600. \\ x = 6 = 15{,}600 & \end{array}$$

Let us contrast these data with those for the corresponding oxide of phosphorus. The compound P_2O_3 dissolves in water with considerable evolution of heat. The thermal data observed when soda is added to this solution are summed up as follows:—

$$[P^2O^3Aq,\ x\ NaOHAq]$$

$$\begin{array}{ll} x = 1 = 14{,}800 & \\ & \text{diff.} = 13{,}700 \\ x = 2 = 28{,}500 & \\ & \ \ '' \ \ = \ \ 400. \\ x = 3 = 28{,}900 & \end{array}$$

Aqueous solutions of As_2O_3 and P_2O_3 are therefore altogether different as regards reaction, and hence also as regards composition. It is very probable that As_2O_3 dissolves unchanged in water, but it is nearly certain that an aqueous solution of P_2O_3 contains the acid H_3PO_3. But a comparison of the heats of neutralisation of aqueous solutions of As_2O_5 and P_2O_5 shews that these liquids are very analogous; each indeed contains a tribasic acid. Thus,

$$\begin{array}{llcll} \multicolumn{2}{l}{[H^3PO^4Aq,\ x\ NaOHAq]} & \quad & \multicolumn{2}{l}{[H^3AsO^4Aq,\ x\ NaOHAq]} \\ x = 1 = 14{,}800 & & & x = 1 = 15{,}000 & \\ & \text{diff.} = 12{,}300 & & & \text{diff.} = 12{,}600 \\ x = 2 = 27{,}100 & & & x = 2 = 27{,}600 & \\ & \ \ '' \ \ = \ \ 6{,}900 & & & \ \ '' \ \ = \ \ 8{,}400 \\ x = 3 = 34{,}000 & & & x = 3 = 36{,}000 & \\ & \ \ '' \ \ = \ \ 1{,}300 & & & \ \ '' \ \ = \ \ 1{,}400. \\ x = 6 = 35{,}300 & & & x = 6 = 37{,}400 & \end{array}$$

89. Too much stress must not be placed on any scheme of chemical classification of acids founded solely on thermal data. It is very probable that a considerable portion of the heat evolved during the neutralisation of acids by bases indicates physical, rather than chemical, change. If this is forgotten, very contradictory conclusions may be drawn from thermal data regarding the chemical composition of apparently analogous compounds. Thus, we have seen that Thomsen assigns analogous

formulæ to arsenic and phosphoric acids viz. $HPO_3(OH)H$ and $HAsO_3(OH)H$; he has also assigned the formula $HPO_2(OH)H$ to phosphorous acid, and he thinks his data shew that an aqueous solution of arsenious oxide does not contain arsenious acid but the unchanged oxide As_2O_3, but on the other hand that an aqueous solution of arsenic oxide contains the acid H_3AsO_4. Now an alkaline solution of arsenious oxide is quickly oxidised by addition of iodine, but an aqueous solution of the same oxide is not oxidised by this means. Thomsen[1] gives these numbers:—

$[As^2O^3Aq, I^4, 4NaHCO^3Aq] = 114{,}200$; but $[As^2O^3Aq, I^4] = -5{,}780$.

An aqueous solution of phosphorous oxide is very slowly oxidised by iodine, although the thermal value of the reaction is a large positive quantity:

$$[P^2O^3Aq, I^4] = 71{,}400.$$

Thomsen suggests, that in the oxidation of aqueous As_2O_3 it is only necessary to add on oxygen and water, but that in the oxidation of aqueous P_2O_3 it is necessary to bring about some more profound change in the arrangement of the constituent parts of the compound. But Thomsen's previous conclusions, as summarised above, are directly opposed to this view; to convert $HPO_2(OH)H$ into $HPO_3(OH)H$ should be a simpler process than to produce $HAsO_3(OH)H$ from As_2O_3 and H_2O.

90. Thomsen has considered the thermal phenomena attending the neutralisation of a few acids in considerable detail. Let us look at his treatment of the thermal changes accompanying the action of alkalis on a solution of periodic acid[2].

91. Periodic acid, H_5IO_6, is produced by the mutual action of perchloric acid, iodine, and water; thus,

$$H_2Cl_2O_8 + I_2 + 4H_2O = 2H_5IO_6 + Cl_2.$$

When chlorine is passed into a strongly alkaline solution of sodium iodate, sodium periodate is obtained; thus,

$$NaIO_3 + Cl_2 + 3NaOH = Na_2H_3IO_6 + 2NaCl.$$

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[1] *Loc. cit.* 2. 237.

[2] *Loc. cit.* 1. 244.

Barium periodate is produced by heating barium iodate; thus,

$$5BaI_2O_6(\text{heated}) = Ba_5(IO_6)_2 + 4I_2 + 9O_2.$$

The compound H_5IO_6 is the only periodic acid which has been obtained, but salts are known which appear to be derived from other acids. Thus Ag_5IO_6 (obtained by adding $AgNO_3$ to solution of $Na_2H_3IO_6$ or $Ba_5(IO_6)_2$) dissolves in nitric acid, and the salt $Ag_2I_2O_8$ separates from this solution;

$$(? \; 2Ag_5IO_6 + 8HNO_3 = Ag_2I_2O_8 + 8AgNO_3 + 4H_2O).$$

When $Ag_2I_2O_8$ is treated with water it is separated into periodic acid and a new silver salt $Ag_4I_2O_9$; thus,

$$2Ag_2I_2O_8 + 5H_2O = Ag_4I_2O_9 + 2H_5IO_6.$$

92. The following are the thermal data obtained by Thomsen regarding the neutralisation by potash of the acid H_5IO_6:—

n	$[H^5IO^6Aq, nKOHAq]$
1	5,150
$\frac{3}{2}$	16,520
2	26,590
$\frac{5}{2}$	28,230
3	29,740
5	32,040.

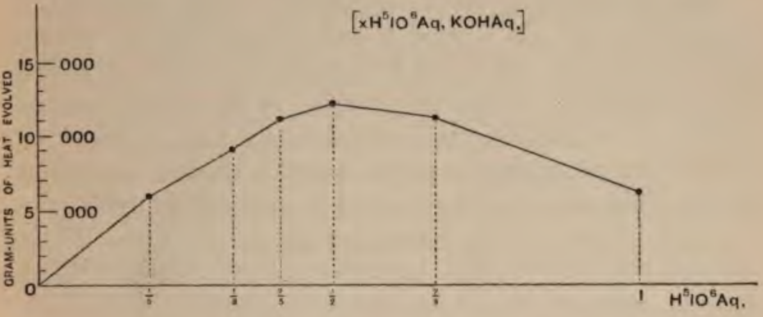
The action of the first formula-weight of potash added is attended with evolution of 5,150 units of heat
„ of the second do. do. 21,440 „ „
} sum = 26,590; = 13,295 units per KOH added.
„ of the third do. do. 3,150 „ „
„ of the fourth & fifth do. 2,300 „ „

The mean heat of neutralisation of most acids per formula-weight of potash or soda added is about 13,500 gram-units; but no acid shews so great a difference between the thermal values of the action of the first and second quantities of alkali as periodic acid. Thomsen's results, when the quantity of acid varies that of potash being constant, are as follows:—

n	$[nH^5IO^6Aq, KOHAq]$
$\frac{1}{5}$	6,410
$\frac{1}{3}$	9,910
$\frac{2}{5}$	11,290
$\frac{1}{2}$	13,300
$\frac{2}{3}$	12,010
1	5,150.

The quantity of heat evolved reaches a maximum when the acid and base react in the proportion H_5IO_6 : 2KOH. This proportion of potash indicates what Thomsen calls the 'limit of normal neutralisation' of the acid H_5IO_6.

The results contained in the foregoing table are shewn in graphic form in the accompanying figure. The process of neutralisation evidently proceeds regularly until the proportion $\frac{1}{2}H_5IO_6 : KOH$ (or $H_5IO_6 : 2KOH$) is reached. When more acid is then added much heat is absorbed; 8,150 units being the quantity absorbed by addition of another $\frac{1}{2}H_5IO_6$ grams of acid. This absorption of heat points to the production of an acid potassium salt in the solution.



Analogous phenomena are exhibited by various dibasic acids; thus when H_2SO_4 (grams) is added to K_2SO_4 (grams) in solution, 935 gram-units of heat are absorbed; when H_2SeO_4 is added to K_2SeO_4, 290 units are absorbed; and when $H_2C_2O_4$ is added to $K_2C_2O_4$, 432 units are absorbed; in each case an acid salt is produced.

93. These facts regarding periodic acid point to the conclusion that the normal potassium salt of the acid H_5IO_6 must have the formula $K_2H_3IO_6$, and the acid salt the formula KH_4IO_6. Two-fifths of the total hydrogen in the acid is, on this view, normally replaceable by potassium.

But how are we to account for the existence of the salts $Ag_4I_2O_9$, $K_4I_2O_9$, &c.? Here we must remind ourselves that many periodates of the form $X_2H_3IO_6$ easily lose water, on heating, with production of new salts $X_4I_2O_9$. To indicate the

6—2

easy occurrence of this reaction it will be advisable to double the ordinary formula for periodic acid, and to write it $H_{10}I_2O_{12}$. This acid will then be regarded as tetrabasic, forming the acid salts $X_2H_2 . H_6I_2O_{12}$, and the normal salts $X_4 . H_6I_2O_{12}$ some of which readily lose water ($3H_2O$) with production of salts of the form $X_4I_2O_9$; these last named salts may then be regarded as derived from an acid $H_4I_2O_9$ ($= H_4 . H_6I_2O_{12} - 3H_2O$).

But, remembering that when 2KOH is added to $H_4 . H_6I_2O_{12}$ the quantity of heat evolved is only a small fraction of that produced when 4KOH is added to the same quantity of acid, it occurs to us to ask: is the salt produced by the mutual action of 2KOH and $H_4 . H_6I_2O_{12}$ really the acid salt $K_2H_2 . H_6I_2O_{12}$? It has been suggested that the salt in question has the composition $K_2I_2O_8$. This salt ($K_2I_2O_8$) is, we know, produced when chlorine is passed into an alkaline solution of potassium iodate. If the action of 2KOH on $H_4 . H_6I_2O_{12}$ results in the production of $K_2I_2O_8$, but the action of 4KOH on the same quantity of the same acid results in the production of $K_4 . H_6I_2O_{12}$, then the action of the acid on the last mentioned salt would probably result in the formation of the first named salt, viz. $K_2I_2O_8$. On this view, these three reactions would be represented in formulæ thus:

(1) $2KOH + H_4 . H_6I_2O_{12} = K_2I_2O_8 + 6H_2O$;

(2) $K_2I_2O_8 + 2KOH + 2H_2O = K_4 . H_6I_2O_{12}$;

(3) $K_4 . H_6I_2O_{12} + H_4 . H_6I_2O_{12} = 2K_2I_2O_8 + 8H_2O$.

In (1) we have not only partial neutralisation of the acid but also the separation of $6H_2O$; in (2) we have fixation of $2H_2O$ accompanying the production of the new salt; and in (3) we have separation of $8H_2O$ accompanying the decomposition of the normal salt. We should expect reaction (1) to be accompanied by the evolution of less heat than (2), and we should certainly expect reaction (3) to occur with absorption of a considerable quantity of heat; and these expectations are confirmed by the data given in the tables on p. 82.

94. Perhaps if we write the formula of periodic acid, with Thomsen, as $H_4I_2O_9 . 3H_2O$ rather than $H_4 . H_6I_2O_{12}$, we get as good a general view of the facts regarding the periodates as can be hoped for at present. The action of potash on this acid would be formulated in this way:—

(1) $H_4I_2O_9 . 3H_2O + 2KOH = K_2I_2O_8 + 6H_2O$;

(2) $K_2I_2O_8 + 2H_2O + 2KOH = K_4I_2O_9 . 3H_2O$.

Reaction (1) is attended with the evolution of 2 × 5,150 units of heat; reaction (2) with the evolution of 2 × 21,440 units. Taking the mean thermal value of 2KOH as 2 × 13,300, it is seen that reaction (1) is 2 × 8,150 units less, and reaction (2) is 2 × 8,140 units more, than the mean[1].

95. A thermal examination of the neutralisation-phenomena of silicic acid has been made by Thomsen[2]. The solution used was prepared by exactly neutralising an aqueous solution of sodium silicate of known strength by hydrochloric acid. Thomsen's general results are as follows:—

(1) Silicic acid exhibits no fixed neutralisation-point.

(2) The heat of neutralisation increases as the quantity of acid increases, and approaches a probable maximum, equal to 13,400 units for one formula-weight of soda.

(3) When the quantity of silicic acid remains constant, and is equal to that expressed by the formula SiO_2, the thermal value of the action of soda increases as the quantity of soda increases, and approaches a probable maximum of 6,300 gram-units.

(4) The thermal value of the gelatinising of an aqueous solution of silicic acid is almost *nil*.

(5) The thermal phenomena attending the mutual action of soda and silicic acid point to the existence, under certain conditions, of isomeric modifications of the acid.

Thomsen has shewn that sulphydric acid is a monobasic acid: HSH. The analogies between the actions of sulphur and oxygen lead him to favour the view that water is also a monobasic acid: HOH; the salts Na_2S and K_2S cannot exist in aqueous solution, no more can the salts Na_2O and K_2O exist in aqueous solution. This view helps to throw some light on the anomalous behaviour of an aqueous solution of silicic acid towards soda. The base (soda) is divided between the two acids (silicic acid and water) in accordance with the relative avidities[3] (or affinities) of these acids. The avidity of most acids is so much greater than that of water, that when an acid and

[1] For more details see Thomsen, *loc. cit.* **1.** 252—3.

[2] *Loc. cit.* **1.** 211, *et seq.*

[3] See *post*, pars. 102—110.

water react on a base the whole or almost the whole of the base is combined with the acid; but the avidity of silicic acid is so small (almost equal to nothing according to Thomsen) that a considerable quantity of the base remains combined with the water. For this reason, also, the heat evolved in the action under consideration varies considerably, according as much or little water is present.

96. We must now turn to Thomsen's treatment of the thermal phenomena presented during the neutralisation of bases.

The action, the thermal value of which is to be measured, may be represented by the general formula

$$[BAq, H^2SO^4Aq],$$

where B is a base.

When the product of the action is an insoluble salt, e.g. when B = SrO or BaO, the thermal value of the precipitation of this salt from solution must be determined.

Thomsen gives the following numbers as representing the values of the reaction formulated above when the base varies:—

Base	Gram-units +.	Base	Gram-units +.	Base	Gram-units +.
Li_2O	31,288	Tl_2O	31,095	BaO	36,896
Na_2O	31,378	$(NH_4)_2O$	28,152	SrO	30,710
K_2O	31,288			CaO	31,140.

None of these numbers, with the exception of those for ammonia and baryta, differs much from that for soda, viz. 31,378. An aqueous solution of ammonia certainly differs very considerably from an aqueous solution of any of the other oxides examined. The large value obtained for baryta is explained by the fact that barium sulphate is precipitated, and that heat is evolved in this process. But strontium sulphate is also an insoluble salt: why is the value observed for strontia less than that observed for soda? Thomsen answers this question by saying that heat is absorbed when strontium sulphate is precipitated from its solution. The mode of reasoning on experimentally determined data by which this result is arrived at is instructive. Let us examine it a little.

97. In the first place, Thomsen compares the heats of neutralisation of soda and baryta when acted on by various

acids which form soluble salts with both bases, with the heats of neutralisation of these bases when acted on by sulphuric acid.

The following table contains his results[1]:—

		Heat evolved by the action of			
Acid.		$2NaOH$	$Ba(OH)_2$	*Difference.*	
Hypophosphorous	$2H_3PO_2$	30,320	30,931	611	mean = 507, or about 2 per cent. of the heat of neutralisation.
Chloric	$2HClO_3$	27,518	28,056	538	
Hydrochloric	$2HCl$	27,488	27,784	296	
Nitric	$2HNO_3$	27,364	28,264	900	
Dithionic	$H_2S_2O_6$	27,072	27,760	688	
Ethylsulphuric	$2C_2H_5HSO_4$	26,926	27,560	634	
Acetic	$2C_2H_4O_2$	26,790	26,904	114	
Sulphydric	$2HSH$	15,476	15,748	272	
Sulphuric	H_2SO_4	31,378	36,896	5,518.	

There can be little doubt that the large difference in the last line of this table is due to the heat evolved during the precipitation of barium sulphate, and that the true heat of neutralisation of baryta is approximately the same as (probably about 500 units more than) that of soda[2].

This result is confirmed by a thermal study of the reaction

$$[M^2SO^4Aq,\ BaO^2H^2Aq]$$

where $M = Na$, K, Tl, or NH_4. This reaction if thermally expanded, represents the difference between the heat of neutralisation of baryta and that of soda, potash, thallia, or ammonia, by sulphuric acid;

$$[M^2SO^4Aq,\ BaO^2H^2Aq] = [BaO^2H^2Aq,\ H^2SO^4Aq] - [M^2O^2H^2Aq,\ H^2SO^4Aq].^3$$

The differences as thus measured are shewn to agree very closely with the differences obtained by direct observation of the heats of neutralisation, by sulphuric acid, of baryta and the four bases already named[4].

The two following reactions are strictly comparable,

(1) $[BaCl^2Aq,\ Na^2SO^4Aq] = 5{,}240$; (2) $[SrCl^2Aq,\ Na^2SO^4Aq] = -300$.

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[1] *Loc. cit.* 1. 329.

[2] Therefore, the heat of precipitation of $BaSO_4$ is about 5000 +.

[3] We suppose the sulphate to be separated into $M_2O_2H_2Aq$ and H_2SO_4Aq; the heat absorbed in doing this will evidently be equal to that evolved in the neutralisation of the base $M_2O_2H_2Aq$.

[4] Id. *loc. cit.* 1. 315.

If these reactions are thermally expanded, each is found to consist of four parts; thus (let X = Ba or Sr)

$$[\mathrm{XCl^2Aq,\ Na^2SO^4Aq}]$$
$$= \begin{cases} \underset{(1)}{[\mathrm{XO^2H^2Aq,\ H^2SO^4Aq}]} - \underset{(2)}{[\mathrm{XO^2H^2Aq,\ 2HCl\,Aq}]} \\ - [\mathrm{Na^2O^2H^2Aq,\ H^2SO^4Aq}] + [\mathrm{Na^2O^2H^2Aq,\ 2HCl\,Aq}]. \end{cases}$$

In both cases an insoluble sulphate is produced and precipitated; then, assuming that the true values of (1) and (2) are the same whether X = Ba or Sr, it follows that the difference between the observed values of the two reactions must approximately represent the difference between the heats of precipitation of the two insoluble sulphates. Now 5,240 − (− 300) = 5,540. But the heat of precipitation of barium sulphate has been shewn to be about 5,000 units; therefore the heat of precipitation of strontium sulphate is represented by a small negative value, which is approximately equal to 500 units.

98. Thomsen concludes that the heat of neutralisation of aqueous solutions of the alkalis (including thallia) and alkaline earths, is a constant number: when sulphuric acid is used the value is 31,150 units, when nitric or hydrochloric acid is employed the value is 27,640 units. To this group belong the ~~organic~~ bases $\mathrm{N(CH_3)_4OH}$, $\mathrm{(C_2H_5)_3SOH}$, and $\mathrm{Pt(NH_3)_4(OH)_2}$. The heat of neutralisation of ammonia in aqueous solution is approximately 3,046 units less than that of the alkalis and alkaline earths.

99. Thomsen then proceeds to determine the heats of neutralisation by sulphuric acid of the bases MgO, MnO, NiO, CoO, FeO, CdO, ZnO, and CuO. The method employed consists in decomposing aqueous solutions of sulphates of magnesium, manganese &c. by baryta water; that is to say, values are found for the reaction

$$[\mathrm{MSO^4Aq,\ BaO^2H^2Aq}],$$

where M = Mg, Mn &c.

When this reaction is expanded it becomes

$$[\mathrm{MSO^4Aq,\ BaO^2H^2Aq}] = [\mathrm{BaO^2H^2Aq,\ H^2SO^4Aq}] - [\mathrm{MO^2H^2Aq,\ H^2SO^4Aq}].$$

Hence if the value of this reaction for each base is subtracted from the thermal value of the action of $\mathrm{H_2SO_4Aq}$ on $\mathrm{BaO_2H_2Aq}$, viz. 36,896 units, the remainder represents the heat of neutralisation of the given base by sulphuric acid. The data are presented in the following table[1].

Heats of neutralisation of the bases of the magnesia group.

M	$[BaO^2H^2Aq, H^2SO^4Aq]$	$- [MSO^4Aq, BaO^2H^2Aq]$	$= [MO^2H^2Aq, H^2SO^4Aq]$.
Mg	36,896	5,840	31,056
Mn	„	10,304	26,592
Ni	„	10,628	26,268
Co	„	12,224	24,672
Fe	„	12,004	24,892
Cd	„	13,072	23,824
Zn	„	13,428	23,468
Cu	„	18,456	18,440.

The heat of neutralisation of magnesia is practically the same as that of the alkalis and alkaline earths; the heats of neutralisation of the other bases of the group shew considerable differences.

100. The value of the reaction $[Fe^2O^6H^6Aq, 6HClAq]$ is obtained by Thomsen from the following data:—

(1) $[6NaOH\,Aq, 6HCl\,Aq] = 82,464$; (2) $[Fe^2Cl^6Aq, 6NaOHAq] = 49,008$.

Now reaction (2) when expanded becomes

$$[6NaOH\,Aq, 6HCl\,Aq] - [Fe^2O^6H^6\,Aq, 6HCl\,Aq].$$

Hence from the numbers given

$$[Fe^2O^6H^6\,Aq, 6HCl\,Aq] = 33,456 \text{ units.}$$

101. Thomsen thinks that the true heats of neutralisation of aqueous solutions of the bases of the magnesia group are represented by a constant number, and that the differences observed in his method of procedure are due to differences in the heats of solution in water of the various bases. The arguments by which Thomsen seeks to establish this conclusion are, it seems to me, very untrustworthy[2].

For data regarding heats of neutralisation of acids and bases see Appendix III.

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[1] Thomsen, *loc. cit.* 1. 339—340.

[2] See *loc. cit.* 1. 436—440.

SECTION III. *Distribution of a base between two acids. Relative avidities of acids.*

102. When two acids and one base react in equivalent quantities in a dilute aqueous solution, the products of the action being all soluble in water, what are the proportions in which the acids combine with the base?

103. Neutralisation of various acids by the same base is attended with evolution of different quantities of heat. If one acid replaces another from its combination with a given base the operation will be attended by a thermal change, the value of which will be positive or negative according as the heat of neutralisation of the free acid is greater or smaller than that of the acid already combined with the base.

Thus, consider the reaction between equivalent quantities of nitric acid and sodium sulphate in dilute aqueous solution. The distribution of the various compounds before and after the reaction will be represented thus,

$$Na_2SO_4 + H_2N_2O_6 = x\,Na_2N_2O_6 + x\,H_2SO_4 + (1-x)\,Na_2SO_4 + (1-x)\,H_2N_2O_6.$$

In order to determine the thermal values of the various parts of this reaction it will be necessary to measure the thermal change which occurs during each of the following operations:—

(1) Neutralisation of sulphuric acid by soda.
(2) Neutralisation of nitric acid by soda.
(3) Action of sulphuric acid upon sodium sulphate.
(4) Action of nitric acid upon sodium nitrate.
(5) Action of sulphuric on nitric acid[1].

104. When equivalent quantities of nitric acid and sodium sulphate react in dilute aqueous solution heat is absorbed; but when sulphuric acid and sodium nitrate react under similar conditions heat is evolved. But the final distribution of the base between the two acids will be the same in both cases; and moreover, this distribution will be the same as that which results when equivalent quantities of the two acids and the

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[1] See Thomsen, *loc. cit.* **1.** 98 *et seq.*; or, full abstract of Thomsen's original paper in *Phil. Mag.* (4) **39.** 410.

base mutually react. Suppose we start with $Na_2O_2H_2$, H_2SO_4, and $H_2N_2O_6$ (in solution) and allow the system to settle down into equilibrium, we shall have x thermal units evolved or absorbed. But if we start with Na_2SO_4 and $H_2N_2O_6$, or with $Na_2N_2O_6$ and H_2SO_4, we shall get the same distribution of the various bodies when equilibrium is established as we had in the first case. Now as the thermal change which accompanies a definite chemical change is independent of intermediate states of the changing system, it follows that the thermal value of the mutual actions of the three bodies (call them A, B, A′) is the same whether the actions occur simultaneously or one after the other. Hence we have the general statement

$$\begin{aligned}[A, B, A'] &= [A, B] + [AB, A'] \\ &= [A', B] + [A'B, A];\end{aligned}$$

hence $[A'B, A] - [AB, A'] = [A, B] - [A', B]$.

105. Applying this statement to the special case already considered, we say that the difference between the thermal values of the action of H_2SO_4 on $Na_2N_2O_6$ and that of $H_2N_2O_6$ on Na_2SO_4 (all in dilute aqueous solutions) is equal to the difference between the thermal values of the neutralisation of $Na_2O_2H_2$ by H_2SO_4 and by $H_2N_2O_6$.

Now the thermal values observed by Thomsen were these[1]:—

(1) $[Na^2N^2O^6Aq, H^2SO^4Aq] = 576$; $[Na^2SO^4Aq, H^2N^2O^6Aq] = -3{,}504$;
Difference $= 4{,}080$.

(2) $[Na^2O^2H^2Aq, H^2SO^4Aq] = 31{,}378$; $[Na^2O^2H^2Aq, H^2N^2O^6Aq] = 27{,}234$;
Difference $= 4{,}144$.

These differences vary by about 0·2 per cent. of the value of the heat of neutralisation of either acid by soda.

106. Now consider the distribution of the reacting bodies, when one equivalent of nitric acid (A′), one equivalent of sulphuric acid (A), and one equivalent of soda (B), mutually react; or, for the two cases are identical, when one equivalent of nitric acid (A′) acts on one equivalent of sodium sulphate (AB).

The initial and probable final distribution of the various compounds will be represented by the equation

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[1] Thomsen, *loc. cit.* 1. 112.

$$\left.\begin{array}{c} Na_2O_2H_2 + H_2SO_4 + H_2N_2O_6 \\ (B \; + \; A \; + \; A') \\ \text{or} \\ Na_2SO_4 + H_2N_2O_6 \\ (AB + A') \end{array}\right\} = \begin{array}{r} xNa_2N_2O_6 + xH_2SO_4 + (1-x)Na_2SO_4 \\ +(1-x)H_2N_2O_6 \\ \\ (xA'B + xA + (1-x)AB + (1-x)A'). \end{array}$$

But it is possible that some of the products of this change may mutually react; therefore, in order to determine the total thermal value of the above operation, it will be necessary to determine the following partial values:—

(*a*) decomposition of x equivalents of Na_2SO_4 (AB);

(*b*) formation of x equivalents of $Na_2N_2O_6$ (A′B);

(*c*) reaction of x equivalents of H_2SO_4 (A) on $(1-x)$ equivalents of Na_2SO_4 (AB);

(*d*) reaction of $(1-x)$ equivalents of $H_2N_2O_6$ (A′) on x equivalents of $Na_2N_2O_6$ (A′B);

(*e*) reaction of x equivalents of H_2SO_4 (A) on $(1-x)$ equivalents of $H_2N_2O_6$ (A′).

This analysis of the total thermal change may be expressed in an equation thus

$$\begin{aligned} &[Na^2SO^4Aq, H^2N^2O^6Aq] \\ &\quad = x[H^2N^2O^6Aq, Na^2O^2H^2Aq] - x[H^2SO^4Aq, Na^2O^2H^2Aq] + [(1-x) \\ &\quad Na^2SO^4Aq, xH^2SO^4Aq] + [xNa^2N^2O^6Aq, (1-x)H^2N^2O^6Aq] + [(1-x) \\ &\quad H^2N^2O^6Aq, xH^2SO^4Aq]; \end{aligned}$$

or generally

$$[AB, A'] = x([A', B] - [A, B]) + [(1-x)AB, xA] + [xA'B, (1-x)A'] + [(1-x)A', xA].$$

Thomsen has determined the values of the various parts of this thermal change[1]: the following are his results:—

I. $[H^2N^2O^6Aq, Na^2O^2H^2Aq] = 27{,}234.$

II. $[H^2SO^4Aq, Na^2O^2H^2Aq] = 31{,}378.$

III. To find the value of $[(1-x)Na^2SO^4Aq, xH^2SO^4Aq]$ we have these data

$[Na^2SO^4Aq, nH^2SO^4Aq]$

n	observed	calculated by formula (see p. 93).
$\frac{1}{4}$	− 792	− 786
$\frac{1}{2}$	− 1,262	− 1,270
1	− 1,870	− 1,834
2	− 2,352	− 2,356
4	− 2,682.	− 2,750.

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[1] *Loc. cit.* 1. 99—110.

The approximate formula by which the numbers in column 2 were calculated is

$$[\mathrm{Na^2SO^4Aq}, n\mathrm{H^2SO^4Aq}] = -\frac{n}{n + \cdot 8}\, 3{,}300.$$

IV. $[\mathrm{H^2N^2O^6Aq}, x\mathrm{Na^2N^2O^6Aq}] = -78.$

The number -78 is so small that this part of the change may be neglected. The value of the last part (*e.* p. 92) is also very small, and may safely be neglected in the final calculation.

In addition to these data, Thomsen gives the following measurements of the total thermal reaction under consideration:—

n	$[\mathrm{Na^2SO^4Aq}, n\mathrm{H^2N^2O^6Aq}]$
$\frac{1}{8}$	-904
$\frac{1}{4}$	$-1{,}616$
$\frac{1}{2}$	$-2{,}584$
1	$-3{,}504$
2	$-4{,}052$
3	$-4{,}100.$

Hence $[\mathrm{Na^2SO^4Aq}, \mathrm{H^2N^2O^6Aq}] = -3{,}504.$

107. If we now turn back to the equation on p. 92, omit those parts which have very small thermal values, and slightly alter the form of the equation for convenience sake, we shall have

$$\begin{aligned}
&[\mathrm{Na^2SO^4Aq}, \mathrm{H^2N^2O^6Aq}]\\
&\quad = x([\mathrm{H^2N^2O^6Aq}, \mathrm{Na^2O^2H^2Aq}] - [\mathrm{H^2SO^4Aq}, \mathrm{Na^2O^2H^2Aq}])\\
&\quad + (1 - x)\left[\mathrm{Na^2SO^4Aq}, \frac{x}{1 - x}\,\mathrm{H^2SO^4Aq}\right]\\
&\quad = -3{,}504.
\end{aligned}$$

Substituting the observed values we have

$$\begin{aligned}
&[\mathrm{Na^2SO^4Aq}, \mathrm{H^2N^2O^6Aq}]\\
&\quad = x \times -4{,}144 + (1 - x)\left[\mathrm{Na^2SO^4Aq}, \frac{x}{1 - x}\,\mathrm{H^2SO^4Aq}\right]\\
&\quad = -3{,}504.
\end{aligned}$$

If x is taken as equal to $\frac{2}{3}$, the equation becomes

$$\begin{aligned}
[\mathrm{Na^2SO^4Aq}, \mathrm{H^2N^2O^6Aq}] &= \tfrac{2}{3} \times -4{,}144 + \tfrac{1}{3}[\mathrm{Na^2SO^4Aq}, 2\mathrm{H^2SO^4Aq}]\\
&= \tfrac{2}{3} \times -4{,}144 + (\tfrac{1}{3} \times -2{,}352)\\
&= -3{,}546.
\end{aligned}$$

The difference between the observed value ($-3{,}504$) and the calculated value ($-3{,}546$) does not amount to more than 1·5 per thousand of the heat of neutralisation of either acid.

The thermal value of the reverse action, that namely between equivalent quantities of sulphuric acid and sodium nitrate, may be calculated by the equation

$$[Na^2N^2O^6Aq,\ H^2SO^4Aq]$$
$$= (1-x)\,4{,}144 + (1-x)\left[Na^2SO^4Aq,\ \frac{x}{1-x}\,H^2SO^4Aq\right].$$

Putting x as before equal to $\frac{2}{3}$, we get

$$= \tfrac{1}{3} \times 4{,}144 + (\tfrac{1}{3} \times -2{,}352)$$
$$= 597.$$

The observed value of the reaction was 576; the difference between the observed and calculated values amounts to ·7 per thousand of the heat of neutralisation of either acid.

108. Thomsen draws the following conclusions from the results of this investigation:—

(i) When equivalent quantities of soda, nitric acid, and sulphuric acid mutually react in a dilute aqueous solution, two-thirds of the soda combines with the nitric acid, and one-third with the sulphuric acid.

(ii) The striving of the nitric acid to saturate itself with the base (*das Bestreben sich mit der Basis zu sättigen*) is twice as great as that of the sulphuric acid. Nitric acid in aqueous solution is therefore a 'stronger' acid than sulphuric.

The striving of the acids towards neutralisation Thomsen calls the *avidity* of the acids. We shall see I think that it is better to employ the well-known term affinity. Thomsen's word avidity has the same meaning as is assigned to the term affinity in the only working theory of affinity which has yet been suggested.

109. Applying the method sketched above to the study of the mutual action of hydrochloric and sulphuric acids on soda, Thomsen gets the following results:—

$$[Na^2SO^4Aq,\ H^2Cl^2Aq]$$
$$= x\,([H^2Cl^2Aq,\ Na^2O^2H^2Aq] - [H^2SO^4Aq,\ Na^2O^2H^2Aq])$$
$$+ (1-x)\left[Na^2SO^4Aq,\ \frac{x}{1-x}H^2SO^4Aq\right].$$

But $[Na^2O^2H^2Aq,\ H^2Cl^2Aq] = 27{,}480.$

Hence, putting $x = \frac{2}{3}$, the value of the reaction in question

$$= \tfrac{2}{3} \times -3{,}898 + (\tfrac{1}{3} \times -2{,}352)$$
$$= -3{,}382.$$

The observed value − 3,364 differs from the calculated by less than 1 per thousand of the heat of neutralisation of either acid.

The value of the reverse action may be calculated from the equation

$$[Na^2Cl^2Aq,\ H^2SO^4Aq] = (1 - x)\ 3{,}898 + (1 - x) - 2{,}352.$$

And putting $x = \frac{2}{3}$, we get

$$= \tfrac{1}{3} \times 3{,}898 + (\tfrac{1}{3} \times -2{,}352)$$
$$= 515.$$

Observed value = 488.

Hence the *avidity* (affinity) of hydrochloric acid for soda is equal to that of nitric acid for the same base, and is twice as great as that of sulphuric acid[1].

110. The following table summarises Thomsen's results regarding the relative affinities of the acids examined by him.

RELATIVE AFFINITIES[2] (*avidities*) OF ACIDS FOR SODA.

Acid.			*Acid.*		
Nitric	$H_2N_2O_6$	100	Oxalic	$H_2C_2O_4$	24
Hydrochloric	H_2Cl_2	100	[3]Orthophosphoric	$\frac{2}{3}H_3PO_4$	13
Hydrobromic	H_2Br_2	89	Monochloracetic	$2(CH_2Cl . CO_2H)$	9
Hydriodic	H_2I_2	79	Hydrofluoric .	H_2F_2	5
Sulphuric	H_2SO_4	49	Tartaric	$H_2 . C_4H_4O_6$	5
Selenic	H_2SeO_4	45	Citric	$\frac{2}{3}C_6H_8O_7$	5
Trichloracetic	$2(CCl_3 . CO_2H)$	36	Acetic	$2H_4C_2O_2$	3

SECTION IV. *Classification of elements and compounds.*

111. The existence of a definite periodic connection between the heats of combination of various elements with chlorine, bromine, and iodine, and the atomic weights of these

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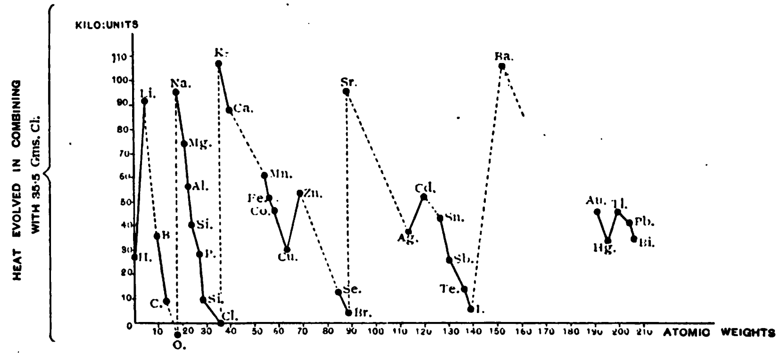
[1] Thomsen, *loc. cit.* 1. 115.

[2] See further, *post*, Chap. v. pars. 225—231.

[3] Taken from a table in Meyer's *Die Modernen Theorien der Chemie*, p. 489 (4th Ed). The number given by Thomsen (*loc. cit.* 1. 308) is calculated for H_3PO_4, a quantity of the acid which is not equivalent to H_2SO_4.

elements, appears to have been first pointed out by Carnelley[1]. Laurie[2] again drew attention to the subject and exhibited the connection in question in a more striking manner by means of a curve.

The following graphic representation, shewing that the heat of combination with chlorine of about thirty elements varies periodically with the variation of the atomic weights of these elements, is based on data taken from Thomsen's *Untersuchungen.* The quantities of heat evolved in the reaction [M, Cl] are stated in kilogram-units, calculated in each case for the combination of one equivalent of chlorine in grams. The numbers are not in every case quite comparable, but the general character of the connection in question is beyond dispute. A broken line indicates want of data.



112. The relations existing between the members of a group of elements are sometimes summarised in the thermal values of comparable reactions undergone by these elements. Thus taking Group II, according to the arrangement of the elements by help of the *periodic law*[3], we have

	Series.							
GROUP II.	4	6	8	3	5	7	9	11
	Ca	Sr	Ba	Mg	Zn	Cd	-	Hg
atomic weights	40	87	137	24	65	112	-	200.

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[1] *Proc. R. S.* **29**. 190.

[2] *Phil. Mag.* (5). **15**. 42.

[3] The student is supposed to be acquainted with the teachings of this law. *The subject is fully* discussed in my *Principles of Chemistry*, Chap. III.

Then tabulating the thermal values of some analogous reactions we have this result:—

	[M, Cl^2, Aq]	[M, Br^2, Aq]	[M, I^2, Aq]
Ca	187,600	165,800	135,300
Sr	195,700	173,800	143,400
Ba	196,300	174,400	144,000
Mg	186,900	165,000	134,600
Zn	112,800	90,900	60,500
Cd	96,300	74,400	44,000
—			
Hg	59,900	?	

These data shew that the thermal value of the change [M, X^2, Aq] increases as the atomic weight of M increases, when M is a metal of an even series belonging to Group II; but decreases as the atomic weight of M increases, when M is a metal belonging to an odd series of the same group.

The difference between the values of [M, X^2, Aq] for each pair of metals is nearly constant.

Thus,

	X = Cl	X = Br	X = I
Ba − Sr =	600	600	600
Sr − Ca =	8,100	8,000	8,100
Ca − Mg =	700	800	700
Mg − Zn =	74,100	74,100	74,100
Zn − Cd =	16,500	16,500	16,500
Cd − Hg =	36,400	?	?

113. The relations existing between change of atomic weight and change of the thermal values of analogous chemical operations are well exhibited by comparing reactions of the four metals, magnesium, calcium, strontium, and barium.

The following data are taken from Thomsen's book[1]:—

M	[MO, H^2O]	[MO^2H^2, Aq]	[MCl^2, $6H^2O$]	[MBr^2, $6H^2O$]
Mg	3,000(?)	0	32,970	
Ca	15,540	2,790	21,750	25,600
Sr	17,700	11,640	18,640	23,330
Ba	22,260	12,260	7,000	9,110
			[$BaCl^2$, $2H^2O$]	[$BaBr^2$, $2H^2O$]

---

[1] Thomsen, *loc. cit.* 3. 555—563.

	$[MN^2O^6, Aq]$	$[M, X^2]$		$[M, O^2, SO^2]$	$[M, O, N^2O^5Aq]$
		X = Cl	X = Br		
Mg	–	151,010	–	231,230	176,480
Ca	3,950	169,820	140,850	247,290	177,160
Sr	– 4,620	184,550	157,700	259,820	185,410
Ba	– 9,400	194,740	169,960	*266,990(?)	*187,020(?)

	$[M, O]$	$[M, O, H^2O]$
Mg	146,000	148,960
Ca	130,930	146,470
Sr	128,440	146,140
Ba	*124,240(?)	*146,500(?)

These numbers, taken along with a few others given by Thomsen (*loc. cit.*), shew that as the atomic weight of the metal increases, in similar compounds of Mg Ca Sr and Ba, there increases also;—

(i) The quantity of heat evolved in the production of MOH_2O from MO; and in the production of MCl_2 and MBr_2 from metal and halogen.

(ii) The solubility of the hydrated oxides in water, and the value of the heat of solution of these compounds.

(iii) The heats of formation (from metal, oxygen, and acid radicle) of the nitrates and sulphates.

The data also shew that increase in the value of the atomic weight of the metal is accompanied by decrease of;—

(i) The value of the heat of formation of MO from metal and oxygen.

(ii) The value of the heat of hydration of the chlorides, bromides, and nitrates.

(iii) The solubility of the same salts in water.

The values of the heats of formation of the hydrated oxides, from metal, oxygen, and water ($[M, O, H^2O]$) seem to be nearly independent of the atomic weight of the metal.

If data similar to the above are tabulated for the alkali metals, it is seen that the generalisation stated for the alkaline earths holds good for the alkali metals also[1].

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* The numbers marked thus are doubtful because the barium used was not free from impurities.

[1] *See* Thomsen *loc. cit.* 3. 564—5.

114. In comparing the losses or gains of energy, as measured by thermal methods, which accompany transformations of matter, we frequently find much difficulty in selecting chemically comparable operations. Suppose we wish to compare the heats of formation of the oxides of phosphorus and nitrogen; we are presented with the following data (Thomsen):—

PHOSPHORUS.	NITROGEN.
$[P^2, O, Aq] = 74{,}520$	$[N^2, O, H^2O] = -30{,}920$
$\left[\frac{P^2, O^3, Aq}{3}\right] = 83{,}353$	$\left[\frac{N^2, O^3, Aq}{3}\right] = -2{,}273$
$\left[\frac{P^2, O^5, Aq}{5}\right] = 81{,}100$	$\left[\frac{N^2, O^5, Aq}{5}\right] = 5{,}964.$

Each number represents the thermal value of the combination of 16 grams of oxygen with phosphorus or with nitrogen. Which values are really comparable? Suppose we are desirous to compare the heat of oxidation of bismuth with the heats of oxidation of phosphorus and nitrogen; we have the number:

$$\left[\frac{Bi^2, O^3, 3H^2O}{3}\right] = 45{,}913.$$

We can scarcely compare this with

$$\left[\frac{P^2, O^3, 3H^2O}{3}\right] = 83{,}440.$$

Bismuthous oxide is insoluble, phosphorous oxide is very soluble, in water.

It may be said that the heats of formation of the highest oxides should always be selected for comparison. If this rule be adopted what shall we say to the following numbers?

$$[Mn, O, H^2O] = 94{,}770, \text{ but } \left[\frac{Mn, O^2, H^2O}{2}\right] = 58{,}165;$$

$$[Sn, O, H^2O] = 68{,}090, \text{ and } \left[\frac{Sn, O^2, H^2O}{2}\right] = 67{,}750;$$

$$[C, O] = 29{,}000, \text{ but } \left[\frac{C, O^2}{2}\right] = 48{,}480;$$

$$[Hg^2, O] = 42{,}200, \text{ but } [Hg, O] = 30{,}670.$$

One oxide is sometimes a solid, another is liquid or gaseous, under the given experimental conditions: or the element to be oxidised is itself a solid and the products are liquids or gases. Even if we seek to compare heats of formation in dilute aqueous solutions, we find that the numbers are not always strictly comparable; in one case the water exerts little or no chemical action on the oxide, in another case the chemical action of the water is more marked than the physical action.

115. In attempting to apply thermal methods to the classification of the elements it is probably best to compare the thermal values of operations, e.g. the action on water or on an acid, wherein various elements act in a similar manner. In some cases it is expedient to compare differences between the heats of formation of two series of compounds.

Let us look at some examples of both methods.

116. Let us compare the differences between the heats of formation of corresponding oxides and chlorides of various metals and non-metals[1].

M	$[M, Cl^2] - [M, O]$	M	$[M, Cl^2] - [M, O, H^2O]$	M	$[M^2, Cl^6] - [M^2, O^3, 3H^2O]$
K_2	–	K_2	73,240	Au	19,610
Na_2	95,620	Na_2	60,000	Fe	310
Tl_2	54,920	Tl_2	51,690	Al	– 22,320
Ag_2	52,860	Ba	48,240		
Hg_2	40,350	Sr	38,410		
Cu_2	24,940	Ca	23,450	Bi	43,520
Ba	70,500	Mg	3,050	Sb	15,360
Sr	56,110	Mn	17,220	As	– 11,910
Ca	38,990	Zn	14,530	P	– 99,720
Pb	32,470	Fe	13,770		
Hg	32,490	Co	13,690		
Cu	14,470	Ni	13,080		
		Cu	14,110		
		Cd	27,560		
		Sn	12,700		

M	$[M, Cl^4] - [M, O^2, 2H^2O]$	M	$[M, Cl^4] - [M, O^2, H^2O]$
Sn	– 6,240	Te	200
Ti	– 38,330	Se	– 10,920
Si	– 48,720		
C	– 74,610		

---

[1] Thomsen, *loc. cit.* 3. 531—533.

M	$[M^2, Cl^{10}] - [M^2, O^5, 3H^2O]$
Sb	$-19{,}040$
P	$-190{,}140$

"When chemically analogous compounds are compared, it appears that the difference between the heat of formation of the chloride and that of the corresponding hydroxide is smaller, the smaller the atomic weight of the positive element." (Thomsen.)

The difference in question is seen to have a positive value in the cases of metals, with the exception of titanium, aluminium, and tin in its highest compounds; and to have a negative value in the cases of non-metals, with the exception of bismuth, antimony in its lowest compounds, and tellurium. Now aluminium hydroxide exhibits feebly acid properties, and the higher hydroxides of titanium and tin form fairly marked metallic derivatives; on the other hand the reactions of the salts of bismuth shew that this element is rather to be classed with the metals than with the non-metals; antimony stands midway between metals and non-metals, and in some of its reactions tellurium shews analogies with metals.

117. Now let us examine the thermal phenomena presented by the action of various elements on water, and on some acids, with the view of classifying these elements[1].

The products of the decomposition of water by metals are in many cases an aqueous solution of the hydroxide of the metal, and hydrogen; e.g.

$$Na_2 + xH_2O = 2NaOHAq + (x-2)\,H_2O + H_2.$$

This reaction would be represented in thermal formulæ as

$$[Na^2, Aq] = -2\,[H^2, O] + [Na^2, O^2, H^2, Aq].$$

If $R = Li_2$, Na_2, K_2 &c. or Ca, Ba, Sr &c. the general thermal equation representing the mutual action of these metals and water will be

$$[R, Aq] = -2\,[H^2, O] + [R, O^2, H^2, Aq].$$

Now the value of $2\,[H^2, O]$ is 136,720 when H_2O represents liquid water.

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[1] Thomsen, *loc. cit.* 3. 542—549.

The following are the values given by Thomsen for the reaction $[R, O^2, H^2, Aq]$[1]

R	$[R, O^2, H^2, Aq]$
Li_2	234,880
Na_2	223,620
K_2	232,920
Tl_2	107,520
Ca	217,620
Sr	226,140
Ba	227,120.

In some cases the products of the mutual action of metal and water are metallic oxide and water, e.g.

$$Fe_3 + xH_2O = Fe_3O_4 + 8H + (x - 4)H_2O.$$

This reaction would be represented thermally as

$$[Fe^3, Aq] = -4\,[H^2, O] + [Fe^3, O^4].$$

If we wish to compare the action of various metals on water from the thermal point of view we ought to tabulate the thermal values of the reactions which actually occur. Unfortunately the data are not sufficient. But let us assume that the products of the action of water and various metals are ROH_2O and H_2; then we may express these actions thermally by the general formula

$$[R, 2H^2O] = -[H^2, O] + [R, O, H^2O].$$

If the value of $[R, O, H^2O]$ is considerably greater than the value of $[H^2, O]$ we may conclude that the metal R will probably decompose liquid water. Thomsen gives these data[2]:—

R	$[R, O, H^2O]$	R	$[R, O, H^2O]$
Mg	148,960	Co	63,400
Mn	94,770	Ni	60,840
Zn	82,680	Cu	37,520
Sn	68,090	Pd	22,710
Fe	68,280	Pt	17,880.
Cd	65,680		

Now as $[H^2, O] = 68{,}360$, it follows that magnesium, manganese, and zinc will probably decompose liquid water without the addition of heat, whereas we should expect tin and iron to decompose hot, but not cold, water. If H_2O represent gaseous water then $[H^2, O] = 58{,}000$; hence, following the foregoing line of argument, it is likely that steam will be decomposed by cadmium, cobalt, and nickel in addition to the metals already enumerated. The metals in the first table on p. 102, except thallium, ought to decompose cold water with evolution of much heat; thallium we should expect would not decompose water even in the form of steam.

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[1] *Loc. cit.* 3. 513.

[2] *Loc. cit.* 3. 513.

118. There are two objections to the use of this kind of argument.

In the first place, the reactions for which thermal values are assigned are in many cases not those reactions which actually occur. In order to classify a given metal as one which would or would not decompose water under specified conditions, we must have more information than purely thermal data can give us: we must know the general chemical analogies of the given metal; we must know the thermal values of the action on water of the analogues of this metal; and we must know the quantities of heat evolved or absorbed during various reactions any of which may possibly occur during the mutual action of the given metal and water.

In the second place, even if the given thermal data really represent the values of reactions which actually occur, and which are strictly comparable, yet these data do not take into account the many physical circumstances which modify the occurrence of the primary chemical change. If the product of the action of a metal on water is easily soluble in water, and the product of the action of another metal is insoluble or only slightly soluble, the mutual action between water and the second metal will occur much more slowly than that between water and the first metal, although the quantity of heat evolved in either reaction may be nearly the same. Again the state of division of the metal will largely influence the action in question. Thus ordinary zinc decomposes water very slowly, but zinc powder much more rapidly; magnesium acts very slowly on water, but magnesium-amalgam quickly decomposes water although there is a considerable evolution of heat during the formation of the amalgam from magnesium and mercury.

119. If the heat of formation of a metallic oxide is only a little greater than that of the formation of water, the course of the chemical change which occurs when the given metal reacts

on hot water, or steam, will be largely conditioned by changes in the relative masses of water and hydrogen. Thus iron decomposes steam forming ferroso-ferric oxide and hydrogen, but this oxide is reduced by hydrogen with production of iron and water. The direction in which this change shall proceed, at any specified temperature and pressure, depends upon the relative masses of steam and hydrogen which are present.

120. In order to compare the actions of metals on each of the three acids, hydrochloric, hydrobromic, and hydriodic, we may tabulate the differences between the heats of formation of metallic chlorides and hydrochloric acid, bromides and hydrobromic acid, and iodides and hydriodic acid respectively. The results are presented in the following table[1]:—

R	$[R, Cl^2] - [H^2, Cl^2]$	R	$[R, Br^2] - [H^2, Br^2]$	R	$[R, I^2] - [H^2, I^2]$
K_2	167,220	K_2	182,180	K_2	166,296
Na_2	151,380	Na_2	163,100	Na_2	144,196
Li_2	143,620				
Tl_2	53,160	Tl_2	74,150	Tl_2	66,396
Hg_2	38,550	Hg_2	59,850	Hg_2	54,476
Cu_2	21,750	Cu_2	41,480	Cu_2	38,556
Ag_2	14,760	Ag_2	36,960	Ag_2	33,636
Au_2	−32,380	Au_2	−8,604	Au_2	−5,004
Ba	150,740	Ba	161,520		
Sr	140,550	Sr	149,260		
Ca	125,820	Ca	132,410		
Mg	107,010				
Mn	67,990				
Zn	53,210	Zn	67,490	Zn	55,266
Fe	38,050				
Co	32,480				
Ni	30,530				
Cu	7,630	Cu	24,140		
Cd	49,240	Cd	66,760	Cd	54,866
Pb	38,770	Pb	56,010	Pb	45,836
Sn	36,790				
Hg	19,160	Hg	42,110	Hg	40,346
$\frac{1}{3}Al_2$	63,320	$\frac{1}{3}Al_2$	71,373	$\frac{1}{3}Al_2$	52,963
$\frac{1}{3}Fe_2$	20,030				
$\frac{1}{3}Au_2$	−28,790				
$\frac{1}{2}Sn$	19,620				

Looking at these data purely from the thermal point of view, the conclusion seems to be that every metal in the table, with the single exception of gold, ought to decompose gaseous hydrochloric, hydrobromic, or hydriodic acid, with production of a chloride, bromide, or iodide. Silver and mercury however do not effect the decomposition of gaseous hydrochloric acid.

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[1] Data from Thomsen.

121. The action of metals on aqueous solutions of the three acids under consideration is somewhat different from that of the same metals on the gaseous acids. The heats of formation of aqueous solutions of the acids are these:—

$[H^2, Cl^2, Aq] = 78{,}360$; $[H^2, Br^2, Aq] = 56{,}752$; $[H^2, I^2, Aq] = 26{,}342$.

When the value of the change $[R, X^2, Aq]$ is greater than 79,000 X_2 being $= Cl_2$, greater than 57,000 X_2 being $= Br_2$, or greater than 27,000 X_2 being $= I_2$, then the metal R will probably decompose a dilute aqueous solution of hydrochloric, hydrobromic, or hydriodic acid.

Thomsen gives these numbers:—

R	$[R, Cl^2, Aq]$
Tl_2	76,960
Pb	75,970
Cu	62,710
Hg	59,860
$\frac{1}{3}Au_2$	4,545.

Thomsen also says that $[R, Cl^2, Aq] < 79{,}000$ when $R = Pt$ or Pd. For the other metals enumerated in the table on p. 104 the value of the reaction in question is greater than 79,000. Now thallium, lead, copper, mercury, gold, platinum, and palladium do not decompose a dilute aqueous solution of hydrochloric acid. But $[H^2, Cl^2, xH_2O]$ becomes less the smaller the value of x; in other words, a concentrated aqueous solution of hydrochloric acid contains more energy than a dilute solution of the same acid. For the most concentrated solutions, $[H^2, Cl^2, Aq]$ is approximately equal to 69,000; such a solution is decomposed by lead.

The quantities of heat evolved when the alkali or alkaline earth metals, magnesium, manganese, zinc, iron, nickel, cobalt, or copper, react on dilute aqueous hydrobromic or hydriodic acid, are the same as when these metals react on dilute hydrochloric acid. The metals in question readily decompose dilute aqueous solutions of hydrobromic or hydriodic acids.

The difference $[R, X^2, Aq] - [H^2, X^2, Aq]$ is greater when $X_2 = Br_2$ than when $X_2 = Cl_2$, and is again greater when $X_2 = I_2$ than when $X_2 = Br_2$, provided R is Tl_2, Pb, Cu, Hg, or Cd. As regards the action of metals on the three acids in question in aqueous solution, cadmium is to be classed with the heavy metals lead, mercury, copper, and thallium.

Thomsen gives the following numbers as representing the quantities of heat evolved, per 2 grams of hydrogen formed, by the action of certain metals on dilute aqueous solutions of any of the three acids hydrochloric, hydrobromic, or hydriodic:—

Mg = 108,300; Al = 79,920; Mn = 49,370; Zn = 34,210;
Fe = 21,320; Co = 16,190; Ni = 15,070; Sn = 2,510.

These numbers fairly represent the relative intensities of the action of the metals enumerated.

122. The thermal data concerning the action of metals on sulphuric and nitric acids may be treated in a manner similar to that adopted in the preceding paragraphs. The general result of such an investigation, so far as the classification of metals is concerned, may be stated thus[1]:—

Thallium, cadmium, mercury, nickel, cobalt, iron, manganese, and zinc should probably decompose dilute sulphuric acid with evolution of hydrogen; the action in the case of thallium being very slow.

Silver and copper should probably not decompose the dilute acid.

Any metal which decomposes a dilute aqueous solution of sulphuric acid with evolution of hydrogen will probably decompose a concentrated solution of the same acid, at certain conditions of temperature, with production of sulphur dioxide and sulphuretted hydrogen.

The nature of the action of copper, mercury, and silver on nitric acid is probably different from that of the action of other heavy metals e.g., zinc, magnesium, cobalt, iron, nickel, manganese, and cadmium. The gaseous products of the action of copper, mercury, and silver are probably to be regarded as the results of direct deoxidation of the acid by the metal; the gaseous products of the action of zinc, iron, cobalt, &c., are probably, for the most part, the results of secondary changes occurring between the acid and hydrogen produced in contact with the acid by the primary action of the metals in question.

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[1] For details see Thomsen *loc. cit.* 3. 547—549; or my *Principles of Chemistry* 270—273. See also Naumann's *Thermochemie* 477—482.

123. If one might venture to found a broad generalisation on the thermal data regarding the action of acids on the heavy metals, one might say that mercury and copper are very distinctly cut off from the other metals, and that lead and thallium shew closer analogies with mercury and copper than with the other metals which have been considered.

124. The application of thermal data to the classification of compounds has been fairly well illustrated by the considerations put forward in pars. 77—101 concerning the neutralisation of acids and bases.

A knowledge of many thermal data is certainly helpful to one who wishes to classify elements and compounds; but a satisfactory classification cannot be based on such data only. We wish to connect changes of energy with changes of chemical configuration. We are still for the most part obliged to interpret the latter changes apart from any precise theory of their mechanism. If we use the terms molecule and molecular actions in speaking of chemical changes in solids and liquids, we employ these terms in a wider and less precise sense than when we apply them to gases and gaseous phenomena.

The data given in Appendices I, III, and V present most of the material available for the thermochemical classification of elements and compounds.

CHAPTER IV.

APPLICATIONS OF THERMAL METHODS TO THE STUDY OF PHENOMENA PARTLY CHEMICAL AND PARTLY PHYSICAL.

125. THE phenomena hitherto considered have all presented physical as well as chemical aspects, but the point of view from which they have been regarded has been as far as possible chemical. We come now to the consideration of certain groups of phenomena which must be studied from the physical standpoint if we wish to grasp their meaning as chemical occurrences.

SECTION I. *Melting, Boiling, Evaporation.*

126. When energy in the form of heat is added to a piece of cold ice, the temperature of the ice increases up to a certain point at which the ice is changed into water. But, provided the heat be added slowly and the pressure remain constant, the temperature of the water remains the same as that of the ice until the whole of the ice is melted. The temperature at which this change occurs is called the melting point of ice. Every solid has a definite melting point.

127. If, after ice has been melted, heat is continuously added to the water which has been produced, the volume of this water increases and its temperature rises until a temperature is reached whereat the water is rapidly changed into steam. If the pressure remains constant, and the heat is slowly added to the water, the temperature of the steam remains the same as that of the water until the whole of the water has been converted into steam. Water becomes water-vapour at any *temperature* and pressure; but for any pressure there is a fixed

temperature, called the boiling point, at which this change proceeds rapidly. If a little water is placed in an exhausted receiver the water quickly evaporates, until the pressure of the vapour in the receiver reaches a certain definite amount, when the evaporation ceases. If now the temperature of the water and vapour is increased, more water becomes vapour, and therefore the pressure of the vapour on the free surface of the water increases. If the temperature is lowered, some of the vapour becomes water, and the pressure of the vapour on the free surface of the water is decreased.

For every temperature, then, there is a definite amount of pressure exerted by the vapour of the water; this is called the vapour-pressure[1] for that temperature.

At each temperature, pressure being constant, there is equilibrium between the water and the vapour of water above it. When such equilibrium exists the vapour is said to be saturated.

The boiling point of water (or of any liquid) is the temperature of the saturated vapour of the water (or of the liquid) when its pressure is equal to the pressure on the free surface of the water (or liquid).

128. When heat is added to steam the volume of the steam is increased, and its temperature rises, until a temperature is reached at which chemical change begins, change, viz., of water-gas into the two elementary gases hydrogen and oxygen. If heat is continuously added, the temperature continues to rise, and the chemical change proceeds more and more rapidly, until about half of the total mass of water-gas is chemically changed, after which the process of change proceeds more slowly, temperature still increasing, until the whole of the water-gas has been changed into oxygen and hydrogen.

The temperature at which this change begins in the case of water-gas is very high, but a similar change can be effected in many other compound gases at much lower temperatures. Thus, gaseous amylic bromide begins to separate into its constituents, amylene and hydrobromic acid, at a temperature of 165°.

The change brought about by the action of heat on water-gas at high temperatures, or on amylic bromide at lower temperatures, is called dissociation. The foregoing sketch indicates that there is a more or less well-marked connection between the phenomena of evaporation and dissociation. This connection will be discussed later on. (See pars. 136, and 145—152.)

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[1] Frequently, but erroneously, called vapour-tension.

129. *Melting.* In order to change a given mass of a solid at a specified temperature into the same mass of liquid at the same temperature, pressure being constant throughout the change[1], a definite quantity of heat must be added to the body. This quantity of heat is called the *heat of liquefaction*, or *heat of fusion*, or *latent heat*, of the solid[2].

The value of the heat of liquefaction of a body may be determined by bringing equal masses of the body, at definite temperatures, one above and one below the melting point, into a calorimeter containing a definite amount of some liquid which dissolves the given solid, and measuring the quantities of heat produced during each process of solution. As in each case the final state of the system is the same, and as the only difference between the initial states is that one system is solid and the other liquid, the difference between the quantities of heat produced (or absorbed) in the process measures the quantity of heat which must be added to the initial solid system to cause it to pass into the initial liquid system.

The following data will serve as examples of the application of this method:—

Hydrated sulphuric acid. Heat of solution in water.

solid $[H^2SO^4H^2O, 400H^2O] = 7{,}120;$

melted $[H^2SO^4H^2O, 400H^2O] = 10{,}800;$

$\therefore$ heat of liquefaction of solid $H_2SO_4H_2O = -3{,}680$ gram-units.

Hydrated sodium chromate. Heat of solution in water.

solid $[Na^2CrO^410H^2O, Aq] = -15{,}800;$

melted $[Na^2CrO^410H^2O, Aq] = -3{,}490;$

hence, heat of liquefaction of $Na_2CrO_410H_2O = -12{,}310$ units.

130. The heat of liquefaction of a solid compound represents the number of gram-units of heat required to convert the mass of the solid expressed by its chemical formula, taken in

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[1] The subject of the connection between change of pressure and change of melting point does not come within the province of this book. We may regard the melting point of a solid as independent of moderate changes of pressure.

[2] The term *heat of liquefaction* is here used as excluding heat of solution.

in grams, into the same mass of liquid, without change of temperature or chemical composition. Very generally however, in such calorimetrical determinations as those just stated, the heat of solution of the solid compound is determined at the ordinary temperature (15 – 20°); in these cases the value given for the heat of liquefaction really represents the quantity of heat required to raise the specified mass of the solid from the stated temperature to the melting point, in addition to the quantity of heat required to melt the solid.

131. When a hydrated salt is melted, quickly cooled, and at once dissolved in water, the heat of solution is, as a rule, less than the number observed by dissolving the solid in water without previous melting and re-solidification. If the melted solid is cooled slowly, the heat of solution is usually unchanged by the process which the body has undergone. It is probable that the process of melting lessens the mutual attractions between the particles of the solid, and if the body is dissolved before these particles have settled down again into their original configurations less work is required to effect solution than is needed when the original state of the solid has been completely restored[1].

132. Ostwald[2] has attempted to measure the amount of chemical change which occurs when two solid salts are fused together, by determining the heats of solution of the individual salts, and of the mixed salts, before and after fusion. Inasmuch as Ostwald observed that a change in the heat of solution sometimes accompanied fusion, when no chemical action between the salts, of the nature of double decomposition, was possible[3],—e.g. K_2CO_3 and Na_2CO_3, or Na_2CO_3 and Na_2SO_4,—he insists on the necessity of arranging the experimental conditions so that change of heat of solution must be due to the occurrence of chemical action between the salts. If one of the two salts used is insoluble this condition is realised, inasmuch as the heat of solution of this salt remains equal to zero throughout the experiment.

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[1] See Nicol. *Phil. Mag.* (5) **15**. 95.

[2] *J. für prakt. Chemie.* (2) **25**. 1.

[3] In such cases Ostwald supposes that double salts are produced by the fusion.

The following numbers will illustrate the method:—

(*a*) 1·835 grams of a mixture, in equivalent quantities, of $BaSO_4$ and K_2CO_3.

(i) Heat of solution before fusion = 6,260 units +,
(ii) " " after " = 5,210 " –.

(*b*) 1·835 grams of a mixture, in equivalent quantities, of $BaCO_3$ and K_2SO_4.

(i) Heat of solution before fusion = 6,460 units –,
(ii) " " after " = 5,460 " –.

Inasmuch as the heat of solution after fusion is in each case practically the same, it follows, according to Ostwald, that the composition after fusion is the same, whether the original mixture consist of $BaSO_4$ and K_2CO_3, or of K_2SO_4 and $BaCO_3$.

Now the complete decomposition of the barium sulphate into barium carbonate would have changed the heat of solution from 6,260 + to 6,460 –, i.e. would have been accompanied by a decrease of 12,720 units. But the actual change was from 6,260 + to 5 210 –, i.e. there was an observed decrease of 11,470 units. Hence, Ostwald concludes, the chemical change spread throughout $\frac{11,470}{12,720} = 90{\cdot}2$, per cent. of the total mass[1].

133. The melting points of many solids have been determined by direct thermometric observations independently of the method based on measurements of the heats of fusion and solution[2].

134. A few generalisations have been ventured on respecting the connections which undoubtedly exist between the melting points and the chemical composition of bodies. These generalisations are wide and somewhat vague; they must be employed with much caution.

The principal generalisations are two:—

I. In a homologous series of carbon compounds, those compounds which have an even number of carbon atoms in their molecules melt at a higher temperature than the neighbouring compounds with an odd number of carbon atoms in their molecules.

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[1] For more details see Ostwald, *loc. cit.*

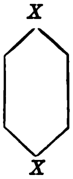
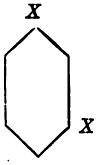
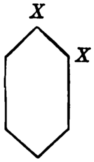
[2] See especially Carnelley, *C. S. Journal*, **14.** 489; **16.** 365; **Trans.** for 1878, 273; **Trans.** for 1880, 125. See also for collected data Carnelley's *Tables of Melting and Boiling Points* (1885).

II. Of any number of isomeric carbon compounds, that one in the molecule of which the atoms are 'most symmetrically and compactly' arranged has the highest melting point.

The following formulæ and melting points serve to illustrate the second generalisation; everything of course depends on the meaning attached to the phrase 'symmetrically and compactly arranged[1].'

	Compound.	*Structural formula.*	*Melting point.*
C_5H_{12}	(1) normal pentane	$CH_3(CH_2)_3CH_3$	liquid.
	(2) iso-pentane	$CH(CH_3)_2CH_2CH_3$	liquid.
	(3) tetramethyl-methane	$C(CH_3)_4$	—20°.
C_8H_{18}	(1) normal octane	$CH_3(CH_2)_6CH_3$	liquid.
	(2) iso-octane	$CH(CH_3)_2(CH_2)_2CH(CH_3)_2$	liquid.
	(3) hexmethyl-ethane	$C_2(CH_3)_6$	96–97°.

Melting points of diderivatives of benzene C_6H_4XX.

	 1 : 4	 1 : 3	 1 : 2	derivatives.
Formula.	*Melting points.* (*C.*)			
$C_6H_4.Cl.Cl$	53°	liq. at - 18°	liq. at - 14°	
$C_6H_4.Br.Br$	89	- 28	- 1	
$C_6H_4.OH.CO_2H$	210	200	156	
$C_6H_4.Cl.I$	56	—	liq.	
$C_6H_4.NO_2.Cl$	83	44	32	
$C_6H_4.NO_2.Br$	126	56	41·5	
$C_6H_4.NO_2.NH_2$	146	110	71	
$C_6H_4.CH_3.CH_3$	15	liq.	liq.	
&c. &c.				

135. *Boiling.* The boiling point of a liquid, as we have already learned, is that temperature at which the pressure of the saturated vapour of the liquid is equal to the pressure on

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[1] See for data and more details, Carnelley, *Phil. Mag.* (5) 13. 110.

the free surface of the liquid. As this temperature necessarily depends on the pressure, the statement of the boiling point of a liquid must be accompanied by a statement of the pressure at which this temperature is determined. If no special pressure is specified, the normal pressure, viz. 760 mm. of mercury, is understood.

In order to change a given mass of liquid at a specified temperature into the same mass of vapour at the same temperature, a definite quantity of energy in the form of heat must be imparted to the liquid. This quantity of heat is called the *heat of vaporisation of the liquid*, or sometimes the *latent heat of the vapour*.

Inasmuch as a liquid is vapourised to some extent at all temperatures, it follows that the heat of vaporisation of a liquid varies according to the temperature at which the change from liquid to vapour occurs. Thus, to convert 1 gram of water at 100° into 1 gram of saturated steam at 100°, 536·5 gram-units of heat must be added to the water; but to convert the same mass of water at 0° into the same mass of water-vapour saturated at 0°, it is necessary to add 606·5 gram-units of heat to the water[1].

136. When heat-energy is added to a liquid, and the liquid is thereby changed into vapour, we know that the energy is not present in the vapour in the form of heat. But we also know that the energy may be regained in the form of heat by causing the vapour to pass again into the state of liquid. What becomes of the energy meanwhile, or in what form it exists in the vapour, we do not know. But the molecular theory of matter supplies us with the outlines of a feasible hypothesis.

This theory regards the molecules of a gas as being in continual motion. Although a value is ascribed to the average velocity of all the molecules in a given volume of a gas, yet the velocity of many individual molecules must very considerably exceed the average velocity. The small particles which build up any portion of a liquid are also regarded by the molecular theory as being in continual motion. The average velocity of these particles, according to the theory in question, is considerably less than that of the molecules of a gas, but at the same time the velocity of some of the particles may be as great as, or greater than, the average velocity of the molecules of the gas which is produced by adding heat to the liquid. If any of these quickly moving particles of a liquid arrive at the surface while they are moving away from the liquid, they will fly off from the free surface of the liquid into the outside space. Addition of heat to the liquid will increase the average velocity of the liquid particles, and hence will increase the velocity of some of the individual particles; the chances that a number of particles should be found, at any specified time, at the surface of the liquid, moving in a direction away from the liquid, will also be increased. Hence the addition of heat-energy will increase the rate at which the liquid passes into the state of vapour.

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[1] Methods for determining boiling points are described in most text books on heat. For special methods and apparatus see Berthelot, *Mécanique Chimique*, **1**. 287. Bunte, *Annalen*, **168**. 139. L. Meyer, *ibid.* **165**. 303. P. T. Main, *Chem. News*, **35**. 59. H. C. Jones, *C. S. Journal*, **Trans.** for **1878**. 175. Carnelley and Williams, *C. S. Journal*, **Trans.** for **1878**. 281. Tables of boiling points will be found in the various articles on Heat in Watts's *Dictionary* and supplements; also, very fully, in Carnelley's *Tables of Melting and Boiling Points*.

On this view of the mechanism of vaporisation, part of the energy which is added to the liquid in the form of heat is used in separating the complex particles of the liquid into less complex particles of the vapour, and part exists in the vapour in the form of energy of the particles which compose that vapour.

While this process is occurring, some of the molecules of the vapour will be driven against the surface of the liquid and will be entangled therein. Some of the vapour, that is to say, will be condensed. The greater the density of the vapour, the greater the amount of condensation that must occur in a given time. When the vapour is so dense that as many molecules of vapour pass into the liquid as particles of liquid pass into the vapour, in a specified time, then the vapour is saturated.

But, according to the molecular theory, evaporation is still proceeding; only it is exactly balanced by the process of condensation. At the temperature at which the vapour is saturated, for a given pressure, the theory asserts that there is as much condensation of vapour as evaporation of liquid in a specified time[1].

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[1] *See Clerk Maxwell, Theory of Heat*, pp. 323-4 (6th Ed.).

Moreover, as we shall learn in a subsequent chapter, there is a considerable amount of evidence in favour of the view that the particles of liquids, or at any rate of many liquids, are built up of groups of molecules, (see definition of molecule in chap. I. par. 27). It is possible that the particles of a chemically homogeneous liquid are of different degrees of complexity, although so many particles may be of the same degree of complexity that we are justified in speaking of the liquid as a homogeneous whole.

If this view is accepted, then a portion of the heat-energy which is added to a liquid during the process of vaporisation is used in separating the more complex into less complex groups of molecules, and also in separating what we have called the *particles* of the liquid, which on this view of the subject are themselves groups of molecules, into the true gaseous molecules which compose the vapour obtained by heating the liquid.

137. The boiling point of a mixture of two liquids which are not mutually miscible, e.g. benzene, or nitrobenzene, and water, is that temperature at which the sum of the pressures of the two vapours is equal to the pressure on the free surface of the liquids. Hence if such a mixture is distilled, e.g. if benzene is distilled in a current of steam, the ratio between the quantities of the two liquids in the distillate is constant, and is equal to the ratio of the products of the density and the pressure of each vapour at the boiling point[1].

138. It is found that the boiling point is not constant in the case of a mixture of two liquids which are miscible in all proportions but between which no chemical action occurs, and also that the composition of the vapour obtained by heating such a mixture of liquids varies in accordance with variations of temperature. Thus, when a mixture of carbon disulphide and benzene in varying proportions is distilled, the boiling point varies, and the ratio of the quantities of these two compounds in the distillate, at any specified temperature, is not the same

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[1] See A. Naumann, *Ber.* **10**. 1421, 1819, 2014, and 2099, (see also Watts's *Dict.* **3rd supp.** 948). Thorpe, *C. S. Journal*, **Trans.** for **1879**. 544. Pierre and Perchot, *Compt. rend.* **73**. 599; **74**, 224. Magnus, *Pogg. Ann.* **38**. 488. *Regnault, Mém. de l'Acad.* **26**. 719.

as the ratio of the products of the density and pressure of each vapour at that temperature[1].

139. So far as experiments have been conducted on the phenomena presented by the boiling and distillation of two liquids mutually miscible and capable of combining chemically with one another, it would appear that when such a mixture is distilled the excess of one liquid which is present, over the quantity required to combine with the other liquid, is removed as vapour, and that the boiling point of the mixture rises until a temperature is reached whereat a compound, composed of both liquids, distils as a whole. The boiling point of this compound of course varies in accordance with the pressure on the surface of the mixed liquids.

Thus when an aqueous solution of hydrochloric acid is distilled, at the ordinary pressure, water vapour passes off until a liquid containing 79·8 per cent. H_2O and 20·2 per cent. HCl remains, which liquid then distils unchanged, the temperature remaining constant at 112°.[2]

140. From what has been said in par. 136 we should expect to find a definite connection between (1) the molecular weight and (2) the chemical composition of liquid compounds and the boiling points of these compounds.

The boiling point of the members of a series of homologous carbon compounds increases as the molecular weight increases. Thus take the series of normal paraffins C_nH_{2n+2}.

Boiling points of normal paraffins.

		B.P.	Difference.
Butane	C_4H_{10}	1°	
Pentane	C_5H_{12}	38	37°
Hexane	C_6H_{14}	70	$32 = 37 - 5$
Heptane	C_7H_{16}	99	$29 = 32 - 3$
Octane	C_8H_{18}	124	$25 = 29 - 4$
Dodecane	$C_{12}H_{26}$	202	$78 = 19{\cdot}5 \times 4$
Hexdecane	$C_{16}H_{34}$	278	$76 = 19 \times 4$

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[1] See F. D. Brown, *C. S. Journal*, **Trans.** for **1879**. 547.

[2] See Roscoe and Dittmar, *C. S. Journal*, **12**. 128: **13**. 146: **15**. 270. Berthelot, *Ann. Chim. Phys.* (5). **4**. 489. On the boiling points of salt-solutions see Nicol, *Phil. Mag.* (5). **18**. 364.

The difference between the boiling points of two consecutive members of this series appears to decrease by about 4° until it attains the value 19°, after which it apparently remains constant.

These numbers, and many more might easily be given[1], are sufficient to shew that the boiling points of the members of a homologous series of liquid carbon compounds do not depend only on the molecular weights of these compounds. The proportion between the numbers of carbon and hydrogen atoms in the normal paraffins, besides the total number of these atoms, appears to influence the boiling points.

Goldstein[2] gives the following formula for finding the boiling point of any normal paraffin of the general form

$$CH_3(CHR')_nCH_3.$$
$$\text{B.P.} = \text{b.p.} + \left(19 + \frac{380}{n(n+1)}\right).$$

B.P. = boiling point required; b.p. = boiling point, and n = number of atoms of carbon in the molecule, of the paraffin next lower in the series than that the B.P. of which is required.

Thus B.P. of

$CH_3.(CH_2)_3.CH_3 = 39°{\cdot}0$; required the B.P. of $CH_3.(CH_2)_4.CH_3$.

$$\begin{aligned}\text{B.P. required} &= 39 + \left(19 + \frac{380}{30}\right)\\ &= 39 + 19 + 12{\cdot}66\\ &= 70°{\cdot}66. \quad \text{B.P. observed} = 70°{\cdot}6.\end{aligned}$$

The same formula appears to hold good for finding the B.P. of any iso-paraffin of the series $CH(CH_3)_2.CH_2R'.CH_3$, given the B.P. of one member of this series.

Thus B.P. of

$CH(CH_3)_2.CH_2.CH_3 = 30°{\cdot}5$; required the B.P. of $CH(CH_3)_2.(CH_2)_2.CH_3$

$$\begin{aligned}\text{B.P. required} &= 30{\cdot}5 + \left(19 + \frac{380}{30}\right)\\ &= 30{\cdot}5 + 19 + 12{\cdot}66\\ &= 62°{\cdot}16. \quad \text{B.P. observed} = 62°{\cdot}0.\end{aligned}$$

141. From the known data regarding the boiling points of isomeric hydrocarbons, it has been concluded that, of any

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[1] See Naumann's *Thermochemie*, pp. 172—177.

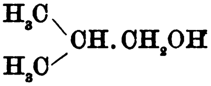
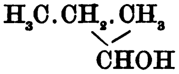
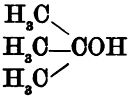
[2] *Ber.* **12.** 689; also *C. S. Journal*, **Abstracts for 1882.** 374 (original paper is *in Russian).*

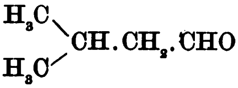
number of isomerides containing only carbon and hydrogen, that one has the lowest boiling point the molecule of which contains, in the language of the theory now in vogue, the greatest number of 'side chains'. Thus,

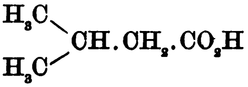
Isomeric Pentanes C_5H_{12}.		B. P.
(1) normal pentane	$CH_3.(CH_2)_3.CH_3$	39°
(2) isopropyl-methyl-methane	$CH_2.CH(CH_3)_2.CH_3$	30·5
(3) tetramethyl-methane	$C(CH_3)_4$	9·5

Isomeric Hexanes C_6H_{14}.		B. P.
(1) normal hexane	$CH_3(CH_2)_4CH_3$	70°·5
(2) isopropyl-ethyl-methane	$CH_2.CH(CH_3)_2.C_2H_5$	62
(3) di-isopropyl	$2CH(CH_3)_2$	58
(4) trimethyl-ethyl-methane	$C(CH_3)_3C_2H_5$	43–48.

Naumann has extended this generalisation to certain oxygenated carbon compounds. He gives the following formulæ and boiling points[1]:—

Butylic Alcohols $C_4H_{10}O$.		B. P.
(1) normal primary	$CH_3.CH_2.CH_2.CH_2OH$	116°
(2) iso-primary	 $\begin{array}{l} H_3C\diagdown \\ \qquad CH.CH_2OH \\ H_3C\diagup \end{array}$	109
(3) normal secondary	 $\begin{array}{l} H_3C.CH_2.CH_3 \\ \qquad \diagdown\diagup \\ \qquad CHOH \end{array}$	89
(4) normal tertiary	 $\begin{array}{l} H_3C\diagdown \\ H_3C—COH \\ H_3C\diagup \end{array}$	82·5

Valeric Aldehydes $C_5H_{10}O$.		B. P.
(1) normal valeric aldehyde	$CH_3.(CH_2)_3.CHO$	102°
(2) ordinary „ „	 $\begin{array}{l} H_3C\diagdown \\ \qquad CH.CH_2.CHO \\ H_3C\diagup \end{array}$	92

Valeric Acids $C_5H_{10}O_2$.		B. P.
(1) normal valeric acid	$CH_3.(CH_2)_3.CO_2H$	185°
(2) ordinary „ „	 $\begin{array}{l} H_3C\diagdown \\ \qquad CH.CH_2.CO_2H \\ H_3C\diagup \end{array}$	175

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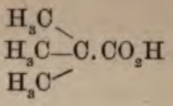
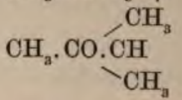
[1] *Ber.* 7. 173. Id. *Thermochemie*, pp. 167—172.

		B. P.
(3) trimethyl acetic acid		161°

Ketones $C_5H_{10}O$.		B. P.
(1) methyl-propyl ketone	$CH_3.CO.C_3H_7$	99°–105
(2) methyl-isopropyl ketone		93·5

142. Naumann[1] also gives data which seem to shew that in many isomeric carbon compounds containing oxygen, that isomeride has the lowest boiling point in which the oxygen atom, (or atoms) is 'situated near the middle of the chain' of atoms which form the molecule. But such an expression as 'near the middle of the chain' conveys no information about the form of a molecule, or the arrangement of atoms in space[2].

143. According to Schall[3] there is a connection between the rate of evaporation, at the boiling point, of a liquid carbon compound and the molecular weight of that compound in the state of gas.

Schall heats the liquids to be examined in their own vapours, and observes the times required for the evaporation of equal volumes; the times required for the evaporation of equal weights are then calculated, the relative densities of the liquids at their boiling points being known.

The time of evaporation of equal weights of liquid compounds, according to Schall's determinations, is inversely proportional to the molecular weights of these compounds.

SECTION II. *Dissociation.*

144. In par. 128 it was stated that by adding heat to steam the temperature of the steam increases, and a point is reached whereat chemical change of steam into hydrogen and

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[1] *Ber.* **7**. 206; and *Thermochemie*, *loc. cit.* See also Watts's *Dict.* **3rd supplt.** pp. 944-5.

[2] On the connections between melting and boiling points and chemical composition see also Mills, *Phil. Mag.* (5). **18**. 173.

[3] *Ber.* **16**. *3011*: **17**. 1044.

oxygen begins. When amylic bromide is heated to 165° change into amylene and hydrobromic acid begins.

We have now to consider the phenomena presented by such changing systems as steam and amylic bromide, chiefly with the view of elucidating the relations between the composition of these systems and the temperature and pressure at which any specified change occurs.

145. The outstanding features of the phenomena connoted by the term *dissociation* are: (1) a change of more complex into less complex compounds, or of compounds into elements, brought about by the action of heat, some or all of the bodies produced being gases; and (2) the possibility of the reversal of the process by cooling the products of the primary change in contact with each other.

146. The following numbers present us with three typical cases of dissociation. In each case a compound is heated, the temperature rises, and the density of the gases decreases. The composition of the original compound is known, as is also the composition of the gaseous compounds produced by the action of heat; hence the amount of chemical change for any temperature-interval can be calculated from observations of the density of the gas.

Dissociation of nitrogen tetroxide[1], N_2O_4.

(Specific gravity of $N_2O_4 = 3·18$; of $NO_2 + NO_2 = 1·59$; (air = 1).)

Temp.	Sp. gr. of gas.	Percentage dissociation.	Mean increase in perctge: dissociation for 10° rise of temperature.
26°·7	2·65	19·96	
35·4	2·53	25·65	6·5
39·8	2·46	29·23	8·1
49·6	2·27	40·04	11·0
60·2	2·08	52·84	12·1
70	1·92	65·57	13
80·6	1·80	76·61	10·4
90	1·72	84·83	8·8
100·1	1·68	89·23	4·4
111·3	1·65	92·67	3·1
121·5	1·62	96·23	3·5
135	1·60	98·69	1·8
154	1·58	100	

[1] *Deville* and Troost, *Compt. rend.* 64. 237.

Dissociation of amylic bromide[1], $C_5H_{11}Br$.

(Specific gravity of $C_5H_{11}Br = 5{\cdot}22$; of $C_5H_{10} + HBr = 2{\cdot}61$; (air = 1).)

Temp.	Sp. gr. of gas.	Percentage dissociation.	Mean increase in perctge: dissociation for 10° rise of temperature.
152°	5·37		
155·8	5·18		
160·5	5·32		
165	5·14	1·6	
171·2	5·16		
173·1	5·18		
183·3	5·15	1·4	
185·5	5·12	2	2·7
193·2	4·84	7·9	7·7
195·5	4·66	12	9·2
205·2	4·39	18·9	
215	4·12	26·7	
225	4·18		4·5
236·5	3·83	36·3	
248	3·30	58·2	
262·5	3·09	68·9	
272	3·11		
295	3·19		1·2
305·3	3·19		
314	2·98	75·1	
360	2·61	100	5·4

Dissociation of amylic iodide[2], $C_5H_{11}I$.

(Specific gravity of $C_5H_{11}I = 6{\cdot}84$; of $C_5H_{10} + HI = 3{\cdot}42$; (air = 1).)

Temp.	Sp. gr. of gas.	Percentage dissociation.	Mean increase, per 10°, of percentage dissociation.
143°	6·05	13·1	
153·5	5·97	14·6	1·4
168	5·88	16·3	1·2
160	5·73	19·4	
210	4·66	46·8	5·5
262	4·38	56·2	1·8

147. The numbers in the third column of these tables are calculated on the assumption that, (1) N_2O_4 dissociates into $2NO_2$; (2) $C_5H_{11}Br$ dissociates into $C_5H_{10} + HBr$; (3) $C_5H_{11}I$ dissociates into $C_5H_{10} + HI$. The sp. gr. of gaseous N_2O_4, $C_5H_{11}Br$, or $C_5H_{11}I$ is readily calculated on the assumption that the

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[1] Wurtz, *Annalen*, **135**. 315.

[2] Wurtz, *Compt. rend.* **62**, 1182: *Annalen*, **135**. 314. See also Naumann's *Thermochemie*, 123.

quantity of each compound expressed by the formula occupies two volumes in the state of gas. Similarly the sp. gr. of a mixture of $NO_2 + NO_2$, $C_5H_{10} + HBr$, or $C_5H_{10} + HI$, is calculated on the same assumption.

Putting $d =$ sp. gr. of the undissociated gas; $D =$ sp. gr. observed; and $p =$ amount of dissociation per cent.; we have[1]

$$p = \frac{100\,(d - D)}{D}.$$

This formula is only applicable when two volumes of the original gas produce four volumes of mixed gases by complete dissociation. If there be x volumes of mixed gases produced from two volumes of the original compound as gas, and if

$$\frac{x}{2} = a,$$

then the equation

$$p = \frac{100\,(d - D)}{(a - 1)\,D}$$

is always applicable.

148. In the cases of dissociation considered it can easily be proved that the compounds N_2O_4, $C_5H_{11}Br$, and $C_5H_{11}I$ exist as gases at low temperatures, and that the gases obtained by heating these to a high temperature actually consist of $2NO_2$, $C_5H_{10}+HBr$, and $C_5H_{10} + HI$, respectively.

But it sometimes happens that little or no direct proof of the occurrence of dissociation is to be had except that presented by the decrease of gaseous density as temperature rises. Thus if solid ammonium chloride is heated, a gas is obtained the density of which is less than that calculated on the assumption that the mass of ammonium chloride represented by the formula NH_4Cl occupies two volumes in the state of gas. But if this gas is allowed to cool ammonium chloride is produced. Now if we assume that NH_4Cl dissociates when heated into $NH_3 + HCl$ we can easily calculate the amount of dissociation at any temperature, from the observed density of the gas. Thus the theoretical density of NH_4Cl gas is 1·86 (air = 1), but the observed density of the gas obtained by heating this compound is less than 1·86, and decreases as temperature rises until at about 500° it is equal to 1·0. The density of a mixture of NH_3 and HCl in equal volumes is 0·93 (air = 1). Hence we conclude that when NH_4Cl is heated it dissociates into $NH_3 + HCl$, and that these gases recombine to produce NH_4Cl as temperature falls.

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[1] *See further* Naumann's *Thermochemie*, 114—115.

A similar phenomenon is presented by the action of heat on phosphorus pentachloride. Data are given in the following table.

Dissociation of PCl_5.[1]

Calculated density of gaseous $PCl_5 = 7{\cdot}2$; of gas consisting of $PCl_3 + Cl_2 = 3{\cdot}6$, (air = 1): amount of dissociation is calculated by the formula $p = \dfrac{100(d-D)}{D}$ on the assumption that 2 volumes of gaseous PCl_5 dissociate into 2 volumes of PCl_3 + 2 volumes of Cl_2.

Temp.	Sp. Gr. of gas.	Percentage dissociation.	Mean increase per 10° of percentage dissociation.
182°	5·08	41·7	3·25
190	4·99	44·3	4·2
200	4·85	48·5	6·3
230	4·30	67·4	6·3
250	4·00	80·0	3·1
274	3·84	87·5	6·2
288	3·67	96·2	0·9
300	3·65	97·3	

149. The resemblance between the course of the change presented by these data and the changes undergone by N_2O_4, $C_5H_{11}Br$, and $C_5H_{11}I$ renders it very probable that these four changes are of the same kind. Hence the conclusion is drawn that the action of heat on PCl_5 presents us with an instance of dissociation.

It has been shewn by Pebal[2] that if the vapour obtained by heating solid ammonium chloride is diffused through a porous plate the diffusate contains considerable quantities of free ammonia. Now if the vapour were really NH_4Cl and not a mixture of NH_3 and HCl, this result appears inexplicable.

Again, Wurtz[3] obtained numbers for the density of phosphorus pentachloride gas at low temperatures nearly agreeing with the calculated density 7·2. The method adopted by Wurtz was to volatilise the vapour of the pentachloride into flasks already containing a known amount of vapour of phosphorus trichloride. From the sum of the weights of the two gases, and from analyses of the contents of the flasks, he calculated the volume and weight of the vapour from the pentachloride, and the pressure under which the vapour existed in each flask. As the mean of 12 experiments, at temperatures ranging from 160° to 175° and pressures varying from 168 to 413 mm., Wurtz obtained the number 7·23 as representing the density of the vapour of phosphorus pentachloride, obtained by gasifying this compound into an atmosphere of phosphorus trichloride[1].

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[1] Cahours, *Compt. rend.* **21.** 625. *Ann. Chim. Phys.* (3) **20.** 369.

[2] *Annalen*, **126.** 193.

[3] *Compt. rend.* **76.** 601.

150. If we refuse to accept the explanation given by the dissociation-hypothesis of the observed variations in the densities of such gases as ammonium chloride, phosphorus pentachloride, &c. then we must fall back on the hypothesis that the coefficients of expansion by heat of these gases are abnormal. The rate of increase of the coefficients of expansion of these gases, on this view, increases as temperature increases, until a maximum is reached, and then again decreases to a constant value. But this explanation is much more far-fetched and contradictory of observed facts than that which is given by the hypothesis of dissociation[2]. Besides this, we shall see that it is possible to frame a consistent theory of dissociation which explains many facts both chemical and physical, and is in keeping with the fundamental laws of energy.

151. On looking at the data presented in the three tables (par. 146) it is seen that the amount of dissociation for a given temperature-interval is at first small, it then increases as temperature rises until about 50 per cent. of the original compound has been dissociated, after which the amount of dissociation decreases for the specified interval of temperature until the change is complete. In these tables the pressure remains at 760 mm. throughout. The temperature at which 50 per cent. of the complete dissociation is accomplished for any specified pressure is called by Naumann, and others, the decomposition-temperature of the given compound. at that pressure.

The course of a dissociation-change is generally conditioned by the pressure, as well as by the temperature, to which the dissociating system is subjected. That this is so in one of the cases already examined is made clear by the following tables[1]:—

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[1] Compare Lemoine, *Études sur les Équilibres Chimiques*, 68—72.

[2] *Compare Naumann's Thermochemie*, 151-2.

Dissociation of N_2O_4.

I. Equal temperatures.

Temp.	Pressure.	Density (air = 1).	Percentage dissociation.
18°	279 mm.	2·71	17·3
18·5	136 „	2·45	29·8
20	301 „	2·70	17·8
20·8	153·5 „	2·46	29·3

II. Equal pressures.

Temp.	Pressure.	Density (air=1).	Percentage dissociation.	Differences (1) of temp.	Differences (2) of dissociation.	Quotient. $\frac{(2)}{(1)}$
− 1°	153 mm.	2·87	10·8	21·8	18·5	0·9
20·8	153·5 „	2·46	29·3			
10·5	163 „	2·73	16·5	11	17·2	1·6
21·5	161 „	2·38	33·7			
14·5	175 „	2·63	20·9	2·3	3·8	1·7
16·8	172 „	2·55	24·7	0·7	1·5	2·1
17·5	172 „	2·52	26·2			
1	138 „	2·84	11·9	17·5	17·9	1·0
18·5	136 „	2·45	29·8	4	5·5	1·4
22·5	136·5 „	2·35	35·3			

III. Equal amounts of dissociation.

Temp.	Pressure.	Percentage dissociation.	Differences (1) of temp.	Differences (2) of pressure.	Quotient. $\frac{(2)}{(1)}$
26°·7	755·5 mm.	19·96	10·7	527	49
16	228·5 „	20·0			
35·4	755·5 „	25·65	18·6	583·5	31·3
16·8	172 „	26·2			
39·8	755·5 „	29·23	19	602	31·7
20·8	153·5 „	29·3			
39·8	755·5 „	29·23	21·3	619	29
18·5	136 „	29·8			
49·6	755·5 „	40·0	27·1	654·5	24·2
22·5	101 „	39·0			

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[1] Naumann, loc. cit. 129—131.

Decrease of pressure, temperature being constant, acts in the same way as increase of temperature when pressure is constant; in both cases the amount of dissociation increases.

Table II. illustrates a point already mentioned, viz. that the amount of dissociation for a given interval of temperature, with a constant pressure, is smaller at low than at higher temperatures, up to a certain limit of temperature.

The fourth and fifth columns of Table III. contain figures which represent equivalent quantities of temperature and pressure, equivalent, that is, as regards their effect on the amount of dissociation. These numbers shew that as the temperature is approached at which 50 per cent. of the original compound is dissociated, the influence on the amount of dissociation of decreasing the pressure is, in this case, much more marked than the effect of increasing the temperature.

152. At any specified temperature there is a certain pressure whereat the process of dissociation stops. This is called the equilibrium-pressure for the specified temperature. If the pressure be decreased, or if the temperature be increased, the change proceeds[1].

A process of dissociation such as we have studied is evidently for the most part conditioned by temperature and pressure only. Is it then possible to treat the subject in a general way so as to arrive at a definite statement of the quantitative relations between temperature, pressure, and amount of dissociation?

153. The relation between the volume of a gas and the pressure to which the gas is subjected may be considered when the conditions are such that (1) the gas is continuously in thermal equilibrium with its surroundings so that any heat produced by compressing the gas at once escapes, and the temperature remains constant; (2) no heat is allowed to enter or leave the gas. In the first case the relation in question may be represented by a series of isothermal lines; in the second case by a series of adiabatic lines. The isothermals represent a scale of temperature; the adiabatics a scale of entropy.

The entropy of a system can change only when heat passes from one part of the system at a higher, to another part at a lower, temperature. Let $H =$ the quantity of heat that so passes from a body at temperature θ_1, measured on the absolute or thermodynamic scale, to a body at temperature θ_2; then the first body loses a quantity of entropy expressed by $\frac{H}{\theta_1}$, and the second body gains a quantity of entropy represented by $\frac{H}{\theta_2}$. But since heat passes only from bodies at higher, to bodies at lower, temperatures, it follows that $\theta_1 > \theta_2$; and therefore

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[1] *But see post*, pars. 155, 160—162.

$$\frac{H}{\theta_1} < \frac{H}{\theta_2}.$$

Hence the entropy of the system is increased by this transference of heat by the amount

$$H\left(\frac{1}{\theta_2} - \frac{1}{\theta_1}\right).$$

The entropy of a body is proportional to the mass; hence it is more accurate to speak of the entropy of unit of mass of a body or system.

The relations between the equilibrium of an isolated gaseous system and the changes of the entropy and energy of that system have been considered by Willard Gibbs[1]. Such a system will be in thermal and mechanical equilibrium when, for a given constant entropy, any change that may occur involves one of two conditions for the energy of the system, viz. (1) the energy increases, or (2) it remains constant.

Consider a mixture of gases some of which can be formed from the others; when the energy of such a system has its smallest value consistent with the entropy and the volume (i.e. when any decrease of the energy must alter the entropy and volume) this system is in what Gibbs calls a 'phase of dissipated energy'; such a phase will be stable.

But the state of a gaseous system is conditioned by six variables:

(1) the masses of the constituents $m_1 \ldots\ldots m_n$,

(2) the volume of unit mass of each constituent $v_1 \ldots\ldots v_n$,

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[1] *Amer. Journal of Sci. and Arts*, (3) **16.** 441; **18.** 277. See also Clerk Maxwell in the *South Kensington Science Conferences*, 1876; also *Theory of Heat*, chaps. VIII. and XI.

(3) the entropy of unit mass of each constituent $\phi_1 \ldots\ldots \phi_n$,
(4) the energy of unit mass of „ „ $\eta_1 \ldots\ldots \eta_n$,
(5) the pressure of each constituent $p_1 \ldots\ldots p_n$,
(6) the temperature „ (thermodynamic scale) $\theta_1 \ldots\ldots \theta_n$.

Changes in the values of any of these variables will be accompanied by changes in the state of the system.

But an ideal system in a 'phase of dissipated energy' has a certain entropy and volume, and has the minimum energy possible for this entropy and volume. For any change of the entropy and volume the energy must still remain at a minimum (or for any change of the energy the entropy must remain at a maximum). Now the energy is conditioned by (1) the volume, (2) the entropy, (3) the masses of the constituents of the system. If the energy is known in terms of these variables, the temperature and pressure can be found in terms of the same variables. But (2) remains always at a maximum: its variation vanishes when energy and volume are constant. Hence an equation can be found between (1) $m_1 \ldots m_n$, (2) $v_1 \ldots v_n$, (3) $\theta_1 \ldots \theta_n$, for each of the two conditions (i) that the energy does not vary, and (ii) that the variation of the entropy vanishes when the energy and volume are constant. The relations of volume, temperature, and mass may be calculated by means of these equations for the assumed conditions of energy and entropy; and an equation may be found to give the density in terms of the temperature and pressure.

In dissociable gases we have 'gas-mixtures with convertible components', i.e. with constituents some of which may be produced from the others. Gibbs assumes that notwithstanding the occurrence of chemical action between the components of such gas-mixtures, the temperature, pressure, volumes, and densities of these dissociable gases are related in the same way as in ideal gas-mixtures with convertible components. Hence the equation which enables the density of an ideal gas-mixture in a phase of dissipated energy to be calculated from the temperature and pressure may be applied to the case of dissociable gases.

The equation in question is given by Gibbs in the following form[1]:—

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[1] *Loc. cit.* **18.** 281.

$$\log \frac{D_1(D-D_1)}{(2D_1-D)^2} = -A' - B' \log t + \frac{C}{t} + \log p\,;$$

where D is the density (air = 1) of the gaseous mixture, D_1 the theoretical density of its less dense component, t the temperature, p the pressure, and A', B', and C are constants to be determined by experiment for each gaseous mixture.

Gibbs has compared the densities of the vapours obtained by heating nitrogen tetroxide, formic acid, acetic acid, and phosphorus pentachloride, at different pressures and temperatures, with the densities calculated by means of this equation. The results shew very close agreement in most cases. Gibbs concludes his paper thus: "The constants of these equations are of course subject to correction by future experiments, which must also decide the more general question—in what cases, and within what limits, and with what degree of approximation, the actual relations can be expressed by equations of such form. In the case of perchloride of phosphorus especially, the formula proposed requires confirmation."

The important point to note with regard to this investigation of Gibbs is that equations are deduced from the fundamental conceptions of the theory of energy as applicable to certain ideal gas-mixtures, and that these equations are found to express, with a fair degree of accuracy, the actual relations between pressure, temperature, and density, in dissociable gases. If the results obtained by Gibbs are confirmed and extended by future experiments we shall have a fairly complete thermodynamic theory of dissociation.

154. But the phenomena of gaseous dissociation may be looked at from the point of view of the molecular theory of matter.

Pfaundler especially has examined the phenomena from this standpoint[1].

According to the kinetic theory of gases there must be differences in the states of motion of individual molecules in a mass of gaseous molecules of one kind. The sum of the kinetic energies of the motion of agitation of the molecules and of the motion of rotation of the parts of the molecules must be a constant quantity as long as temperature remains unchanged, but the distribution of the two motions may differ much, as regards the individual molecules.

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[1] *Pogg. Ann.* **Jubelbd.** 182: and *do.* **131.** 55 *et seq.* (especially pp. 66—71).

Let us call the energy of agitation of the molecules of a gaseous system at constant temperature a, and the energy of rotation of parts of the molecules b; then there are four limiting cases for the distribution of these two energies among the individual molecules of the system. We may have molecules in which

(1) a and b are both at a maximum;
(2) a and b are both at a minimum;
(3) a is at a minimum, and b at a maximum;
(4) a is at a maximum, and b at a minimum.

When two molecules collide, a may be increased at the cost of b, or, as a limiting case, both may remain unchanged. The temperature of individual molecules may be far removed from the mean temperature of the system.

Now suppose heat is added to such a system, the energy of agitation and also that of rotation will increase. The effect will be that some of the molecules will be resolved into their constituent parts; others will be heated to the temperature at which separation into parts occurs, and so on.

The process of separation into parts will proceed rapidly for a time, but, as fewer and fewer molecules remain unseparated, as temperature rises the rate at which the separation proceeds will decrease.

But re-combination of parts of molecules will also be proceeding in the system. The occurrence of this re-combination will be conditioned by the relations between the energies of agitation and of rotation in individual molecules. Only those constituents of molecules will unite which by their union can produce molecules with a rotational energy not greater than that which brings about separation of molecules into parts. If now temperature remain constant, we shall have separation and re-combination proceeding until a state of equilibrium is attained, which will be again disturbed by raising or lowering the temperature[1].

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[1] Dissociation is treated by Pfaundler as a special case of his general theory of 'simultaneous reciprocal reactions in consequence of variations in the motions of individual molecules'.

155. The subject of gaseous dissociation has also been considered from the molecular point of view by J. J. Thomson. In a paper 'On the chemical combination of gases'[1], Thomson treats of dissociation in the light of the theory of vortex-atoms. This theory regards the molecule of a gas as consisting of two or more vortex-rings, which may be separated by a disturbing influence such as the action of heat, light, or electricity, or of other vortex-rings in the neighbourhood. That a compound gas may be different from a mixture of the gases which compose the compound it is necessary that "the mean time during which an atom is paired with another of a different kind, which we shall call the paired time, should be large, compared with the time during which it is alone and free from other atoms, which we shall call the free time." The ratio of paired to free time will be diminished by any disturbance to which the gas is subjected; "if this disturbance is great enough the value of this ratio will be so much reduced, that the substance will no longer exhibit the properties of a chemical compound, but those of its constituent elements." The effect of a disturbance on two vortex-rings may tend to make the connection between the rings stronger, or it may tend to separate the rings; which effect is produced will depend on the direction in which the compound molecule is moving at the time. Molecules may be separated into their constituents by the action of heat, light, electricity &c., or by the effect of high temperature without any external disturbance.

Thomson then considers the conditions under which the ratio of paired to free time is so reduced that the gas separates into its constituents. He considers cases of various degrees of complexity, beginning with that of an elementary gas the molecules of which are diatomic. He shews how an equation is arrived at for such a gas whereby the ratio of the number of free atoms to the number of molecules at any time may be determined. This equation may be expressed as an equation giving the density of the dissociated gas; and the results calculated by it can then be compared with the experimentally determined results (*loc. cit.* pp. 240—241). Further, this form of the equation varies according as it is assumed that the dissociation is produced by collisions between the molecules, or by some external agency such as heat, light, or electricity. In the simple case of iodine vapour "if the dissociation were due to the collisions of the particles, then the paired time would vary inversely as the number of collisions, and...dissociation would be the same at all pressures." But the dissociation of iodine vapour is dependent on the pressure, hence the dissociation is probably not due to collisions between the molecules, but rather to the action of some external agency. In considering the change of gaseous hydriodic acid into iodine and hydrogen it is shewn that the amount of the change, at a given temperature, should be much less dependent on pressure than in the case of iodine vapour. This conclusion follows whether the change is regarded as the effect of collisions between the molecules, or as the effect of an external agency. The experimental results obtained by Lemoine[1] confirm Thomson's theoretical deduction. Other cases are considered in the paper referred to, and equations are deduced whereby the conditions which determine the ratio of paired to free time, and therefore determine the amount of dissociation, may be obtained.

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[1] *Phil. Mag.* (5). **18**. 233.

156. It appears then that two fairly satisfactory theories of gaseous dissociation have been proposed, one founded on thermodynamical considerations, the other developed on the lines of the vortex-atom theory of the structure of matter[2].

157. But what are the phenomena presented by the dissociation of a solid compound into solid and gaseous constituents? Consider the two compounds $AgCl.3NH_3$ and $2AgCl.3NH_3$. If silver chloride is placed in a closed vessel filled with ammonia gas, temperature being about 12°–20°, ammonia is absorbed, the compound $2AgCl.3NH_3$ is produced, and the pressure in the vessel decreases. If more ammonia is now passed into the vessel, absorption again occurs until a certain pressure is attained, when the process stops. If the temperature is now raised, a portion of the compound $2AgCl.3NH_3$ is separated into silver chloride and ammonia. This separation is accompanied with increase of pressure; when a certain pressure is reached the

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[1] See *post*, par. 160.

[2] For a fuller account of the various theories of dissociation see Lemoine's *Études sur les Équilibres Chimiques*.

process ceases. If the temperature is now lowered, ammonia is again absorbed, and the pressure falls, until equilibrium is once more established in the system consisting of xAgCl, y2AgCl . 3NH$_3$, and zNH$_3$.

For every temperature then there is a certain pressure at which neither absorption nor evolution of ammonia occurs, but equilibrium is established. This equilibrium-pressure is independent of the relative amounts of the two solids, AgCl and 2AgCl . 3NH$_3$, present. But suppose the system to be in equilibrium at a specified temperature, say 20°; let the pressure be much increased by pumping a quantity of ammonia into the vessel, absorption will occur and the whole of the silver chloride will be changed into 2AgCl . 3NH$_3$; but the process of absorption will continue, and a new compound AgCl . 3NH$_3$ will be produced. When so much ammonia has been absorbed that the pressure has fallen to a certain amount the process stops. If the temperature is now lowered, more ammonia is absorbed and the pressure falls; if the temperature is raised, ammonia is evolved, and the pressure increases; if the temperature is kept constant and ammonia is pumped into the vessel, a portion of the ammonia is absorbed, and the pressure falls. For every temperature there is a certain pressure at which equilibrium is established in the system consisting of x2AgCl . 3NH$_3$, yAgCl . 3NH$_3$, and zNH$_3$. This equilibrium-pressure is independent of the relative amounts of the two solids 2AgCl.3NH$_3$ and AgCl.3NH$_3$. The following table exhibits the equilibrium-pressures for the interval of temperature 6°–20° for each of the two compounds of ammonia and silver chloride[1].

Temp.	Equilibrium-pressures (in millims. of mercury)	
	2AgCl . 3NH$_3$	AgCl . 3NH$_3$
6°	22	—
7	23·4	—
8	24·9	432
9	26·5	446
10	28·2	465
12	31·9	520
16	40·9	653
18	46·6	723
20	52·6	793

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[1] Hortsman, *Ber.* **9.** 749. See also Isambert, *Compt. rend.* **66.** 1259; **70.** 456.

The difference between the equilibrium-pressures for each system—(i) $x\mathrm{AgCl}, y2\mathrm{AgCl}.3\mathrm{NH}_3, z\mathrm{NH}_3$; and (ii) $x2\mathrm{AgCl}.3\mathrm{NH}_3$, $y\mathrm{AgCl}.3\mathrm{NH}_3$, $z\mathrm{NH}_3$—at any temperature, is so great that it is not difficult to study the relations between pressure, temperature, and amount of chemical change, for either system. But experiments have shewn that in many other cases broadly analogous to this, it is almost impossible to determine the equilibrium-pressures for various temperatures. Take for instance the hydrated salt $\mathrm{CuSO}_4.5\mathrm{H}_2\mathrm{O}$. When a crystal of this compound is heated in a closed vessel, of such a size that the water of the crystal is more than sufficient to saturate the air in the vessel, water-gas is evolved, and the pressure increases; after a time the process stops. If the temperature is now allowed to fall, water is re-absorbed, and the pressure decreases. But the change of pressure is irregular and a long time must elapse before equilibrium is attained. At a moderate temperature the crystal is slowly dehydrated, but at the same time small quantities of water are re-absorbed by parts of the crystal which had before given off water. Irregularities in the form or surface of the crystal largely affect the processes of dehydration and rehydration, and cause fluctuations in one direction or the other. As these fluctuations are accompanied by changes of pressure, it is almost impossible to establish equilibrium, at a specified temperature, in the system consisting of $x\mathrm{CuSO}_4$, $y\mathrm{CuSO}_4.5\mathrm{H}_2\mathrm{O}$, $z\mathrm{H}_2\mathrm{O}$ and varying quantities of other hydrates of CuSO_4. Several processes of dissociation are proceeding simultaneously, and the equilibrium-pressure for any one of the dissociating systems at a constant temperature is so nearly the same as that for the other systems that the establishment of an equilibrium-pressure for the whole system is not attained[1].

If hydrated sodium phosphate, $\mathrm{Na}_2\mathrm{HPO}_4.12\mathrm{H}_2\mathrm{O}$, is heated in a closed vessel, water-gas is given off, and the pressure increases. For any temperature there is an equilibrium-pressure established which is independent of the relative amounts of the dehydrated salt and the various hydrates present. This equilibrium-pressure is the same whether the salt $\mathrm{Na}_2\mathrm{HPO}_4.12\mathrm{H}_2\mathrm{O}$ or a less hydrated salt than this is used, provided the quantity of water in the salt is more than that required by the formula $Na_2HPO_4 . 7H_2O$. If the salt $Na_2HPO_4 . 7H_2O$ is heated, a series of equilibrium-pressures is obtained different from those pressures which characterise the process when a salt is used with any quantity of water more than that required by the formula $Na_2HPO_4 . 7H_2O$ but not exceeding that contained in the salt $Na_2HPO_4 . 12H_2O$. The following numbers represent the results obtained by Debray[1].

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[1] For further details see Naumann, *Ber.* 7. 1573; or *Thermochemie*, 145-6.

Temp.	Equilibrium-pressures	
	Salt with 7 to 12 H_2O.	Salt with less than 7 H_2O.
12°·3	7·4 mm.	4·8 mm.
16·3	8·9 „	6·9 „
20·7	14·1 „	9·4 „
24·9	18·2 „	12·9 „
31·5	30·2 „	21·3 „
36·4 salt melted	39·5 „	30·5 „
40·0	50·0 „	41·2 „

This process presents us with an example of dissociation of a solid body into solid and gaseous constituents intermediate between that exhibited by $CuSO_4 . 5H_2O$ on the one hand, and the pair of salts $2AgCl . 3NH_3$ and $AgCl . 3NH_3$, on the other.

Debray has also studied the action of heat on calcium carbonate[2]. When this compound is heated in a closed vessel lime and carbon dioxide are formed, but, on cooling, calcium carbonate is reproduced. The direction of this change at a red heat is dependent only on the pressure of the gaseous constituent of the system, and is independent of the relative quantities of the solid constituents, lime and calcium carbonate. For each temperature examined there was found to be a maximum pressure exerted by the gaseous carbon dioxide whereat the direct change

$$x\mathrm{CaCO}_3 = \mathrm{CaO} + \mathrm{CO}_2 + (x - 1)\,\mathrm{CaCO}_3$$

stopped. Thus,

Temp.	Equilibrium-pressure.
860°	81 mm.
1040°	520 mm.

When the pressure had become equal to 520 mm. temperature was allowed to fall; carbon dioxide was slowly absorbed and pressure fell, until at 860° it was equal to 81 mm., when the process stopped as long as the temperature was kept at this point. When the temperature was again allowed to fall slowly more carbon dioxide was absorbed, until at about 400° or so the whole of the calcium carbonate originally used had been re-formed.

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[1] *Compt. rend.* **66.** 195.

[2] *Compt. rend.* **64.** 603.

158. A dissociating gaseous system is then, at any temperature, a system in kinetic equilibrium. For each dissociable gas there is a temperature at which the process begins, and another temperature at which it is complete. Pressure being constant, the rate of dissociation increases from the initial temperature until about one-half of the gas is dissociated, and then decreases until the change is complete. The process may be reversed by removing heat from the dissociated system; the temperature falls, and re-combination begins. If the heat produced during the re-combination of portions of the gases were prevented from leaving the system, re-combination would stop, and equilibrium be established; but if the heat is slowly removed, temperature falls continuously, and the process of re-combination proceeds until the initial state of the system is again attained: but the temperature of the system is now rather lower than that at which dissociation began. If the gases produced by dissociation are mixed, combination does not begin until a certain temperature is reached; at this temperature portions of the gases combine, heat is evolved, other portions of the gases combine, and so the operation proceeds. If the temperature at any moment is lowered beyond a certain point, combination stops.

In a chemical decomposition started by the addition of heat-energy, there is also a certain temperature at which the process begins, but, as a rule, the progress of the change is not accompanied by a continuous rise of temperature; if heat is produced it is used in effecting the decomposition of further portions of the system, or it is partly given off to surrounding systems. The rate and amount of a decomposition are independent of pressure, within wide limits; the process is not, as a rule, reversible.

159. Although we can thus contrast the general laws of chemical decomposition with those of dissociation yet we cannot

define either class of changes. Dissociation gradually passes into decomposition. "There is no outline in nature, however convenient or even necessary we may find it to draw one."

Consider the case of hydrated magnesium oxide, $MgO.H_2O$. When this compound is heated it gradually separates into magnesia and water-gas with constant rise of temperature; each temperature is marked by a certain pressure of the water-vapour whereat the process stops; on cooling, the operation is reversed and $MgO.H_2O$ is reproduced. But if the salt is heated to a high temperature and is then cooled, the process is not reversed; the water-gas does not re-combine with the magnesia however great the pressure may be. Dissociation has been succeeded by decomposition.

The action of heat on mercuric oxide presents us with an instance of decomposition; the process is not a function of the temperature when pressure is constant, nor is it a function of the pressure when temperature is constant; neither is it reversible[1].

160. Lemoine[2] has made a very careful study of the conditions which determine the equilibrium of the gaseous system consisting initially of equal volumes of hydrogen and iodine, at 260°, 350°, and 440°. At the highest temperature (440°) the system settles down into equilibrium in about an hour; at 350° equilibrium is established only after some days; and at 260° months elapse before a settled state is attained. The rate of chemical change is also dependent on the pressure at any of the specified temperatures. The composition of the system when equilibrium is attained is scarcely, if at all, conditioned by the pressure, but is dependent almost solely on the temperature. The following numbers present some of Lemoine's results :—

Temperature = 440°.

Pressure.	Percentage of original hydrogen remaining uncombined.
4420 mm.	24
1748 „	25·5
760 „	26
380 „	25
152 „	29

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[1] J. Myers, *Ber.* **6.** 11.

[2] *Ann. Chim. Phys.* (5) **12.** 145 : **26.** 289, especially pp. 304—344.

Temp. = 350°.

3040 mm.	21
1520 „	18·6
*700 „	*18

Temp. = 260°.

*1290 mm.	*63	after 30 days.
*700 „	*85	

The numbers marked with an asterisk are approximate only.

161. These numbers shew how very slowly a settled state is attained by the system at a temperature below 350°. Although the final state at 440° and 350° is only to a small extent conditioned by pressure, yet the influence of pressure on the rate of the change is very marked. This is exhibited by the following numbers:—

Temp. = 350°.

Pressure.	Percentage of hydrogen remaining uncombined	
	After 8 hours.	After 34 hours.
3040 mm.	44	29
1520 „	69	48
760 „	97	61.

The rate of the change varies almost directly as the pressure.

162. If the mass of either the iodine or the hydrogen is increased relatively to that of the other constituent, more hydriodic acid is formed, when everything has settled down into equilibrium, than when the two gases are mixed in the proportion of their atomic weights; but in no case examined did complete combination occur at 440°, and at a pressure varying from about 350 to 1500 mm. The following numbers shew the influence exerted on the final state of the system by increasing the relative mass of hydrogen:—

Temp. = 440°. Pressure = 340 mm.

Proportion of H and I.	Ratio of HI formed to total possible HI.
I + H	·74
I + 2H	·84
I + 3H	·87
I + 4H	·88.

163. This study of the mutual action of hydrogen and iodine is interesting, more particularly as it shews that some processes, which must on the whole be classed as dissociation-phenomena, are much less dependent on variations of pressure, as regards

the equilibrium of the system at any temperature, than those typical processes which we have already considered.

The great slowness with which the system settles down into equilibrium, and the further fact demonstrated by Lemoine that the presence of a porous body, such as spongy platinum, hastens the attainment of this state but does not affect the final composition of the system when equilibrium is attained, shew, I think, that the combination of hydrogen and iodine, or the reverse decomposition of hydriodic acid, presents phenomena which belong at once to those strictly included under dissociation, and also to those included under decomposition and combination.

Lemoine thinks that the amount of dissociation of a gaseous body which is produced from its constituents with condensation is distinctly dependent on pressure as well as on temperature; but that the influence of pressure on the amount of dissociation, at a specified temperature, is small in the case of a gas which is produced from its constituents without condensation. Hydriodic acid belongs to the latter class of gaseous bodies.

164. Thomson's application of the theory of vortex-atoms to the chemical combination of gases points, as we saw[1], to two kinds of dissociation, one in which the influence of pressure is much more marked than in the other. The influence of pressure on dissociation-phenomena stands in need of experimental investigation.

SECTION III. *So-called abnormal vapour-densities.*

165. The term *abnormal vapour-densities* has unfortunately been applied to a class of phenomena most of which are perfectly normal.

That mass of a gaseous compound which is expressed by its formula always occupies two volumes. When N_2O_4 is heated it separates into $2NO_2$: if N_2O_4 occupies two volumes, and NO_2 two volumes, it is evident that the density of the gas obtained by heating N_2O_4 should be one-half of the density of N_2O_4 itself.

The numbers given in the table on p. 121 shew that at about 150° the gas NO_2 exists unmixed with N_2O_4, but that as the temperature falls more and more N_2O_4 is formed. The density of the gas at temperatures lower than those in the table approaches that which would belong to N_2O_4 unmixed with NO_2. If a gas does not dissociate on heating throughout a certain interval of temperature, then, assuming the expansion to be normal, the density must remain constant throughout that interval. If the gas does dissociate there must be a gradual decrease of the density as the temperature rises. Hence the phenomena of dissociation explain such cases of so-called abnormal vapour-densities[1].

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[1] See *ante*, par. 155.

166. The density of the vapour obtained by raising the temperature of a liquid element or compound a little above its boiling point is always found to be greater than that calculated from the chemical formula of the body.

As the temperature rises the density of the vapour decreases, but the calculated density is not attained until a certain temperature, more or less above the boiling-point according to the body examined, is reached.

167. The following tables shew the variations in the densities of several vapours as temperature rises.

(When the pressure is not mentioned it must be understood to be approximately 760 mm.)

Acetic Acid[2].		Butyric Acid.		Anisol.	
Theoretical gaseous density 2·08 (air=1). Boiling point 119°.		Theoretical gaseous density 3·04 (air=1). Boiling point 157°.		Theoretical gaseous density 5·18 (air=1). Boiling point 232°.	
Temperature.	Vapour Density.	Temperature.	Vapour Density.	Temperature.	Vapour Density.
125°	3·20	177°	3·68	245°	5·98
130	3·12	208	3·44	260	5·73
140	2·90	228	3·22	270	5·64
150	2·75	249	3·10	325	5·22
160	2·48	261	3·07	338	5·19
171	2·42	290	3·07		
190	2·30	310	3·07		
200	2·22	330	3·07		
219	2·17				
230	2·09				
250	2·08				
300	2·08				

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[1] For details *regarding individual* compounds see Naumann, Thermochemie *150—154.*

[2] *Cahours, Annalen*, **56.** 176.

FORMIC ACID[1].

Theoretical gaseous density 1·59 (air=1). Boiling point 101°.

Temperature.	Pressure.	Density.	Temperature.	Pressure.	Densi
99°·5	690 mm.	2·52	111°·5	690 mm.	2·2
99·5	662 ,,	2·44	111·5	690 ,,	2·2
99·5	557 ,,	2·34	115·5	649 ,,	2·2
101·0	693 ,,	2·44	115·5	640 ,,	2·1
101·0	650 ,,	2·41	124·5	670 ,,	2·0
105·0	691 ,,	2·35	124·5	640 ,,	2·0
105·0	630 ,,	2·32	184·0	750 ,,	1·6
108·0	687 ,,	2·31	216·0	690 ,,	1·6

WATER[2].

Theoretical gaseous density 0·622 (air=1). Boiling point 100°.

Temperature.	Pressure.	Density.
108°·8	752·7 mm.	0·653
129·1	740·3 ,,	0·633
175·4	764·1 ,,	0·625
200·2	755·9 ,,	0·626

ETHER[2].

Theoretical gaseous density 2·557 (air=1). Boiling point 35°.

Temperature.	Pressure.	Densi
39°·7	762·9 mm.	2·64
46·1	764·5 ,,	2·66
52·2	740·5 ,,	2·63
53·7	745·0 ,,	2·65
66·1	754·3 ,,	2·64
81·1	762·6 ,,	2·61
93·1	762·4 ,,	2·60
102·8	756·2 ,,	2·59
115·3	755·8 ,,	2·57
130·6	756·7 ,,	2·58
132·6	742·5 ,,	2·56
204·5	757·1 ,,	2·56

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[1] Bineau, *Annalen*, **60**. 160.

[2] Horstmann, *Annalen*, **Supplbd. 6**. 63.

PROPYL FORMATE[1].
Theoretical density = 3·04 (air = 1).

Pressure.	Temperature and vapour densities.				
	35°·0	65°·29	80°·15	99°·4	128°
200 mm.	3·2267	2·9892	2·9842	2·9632	2·9708
300 „		3·0181	3·0014	2·9802	2·9780
400 „		3·0469	3·0257	2·9992	2·9884
500 „			3·0490	3·0186	2·9985
600 „			3·0538	3·0258	3·0075
700 „			3·0596	3·0299	3·0150
800 „				3·0340	3·0230

BROMINE AND CHLORINE.

Temp. measured in degrees above boiling point of		Density (air = 1).		Deviation of density from normal, in percentages of the latter.	
BROMINE.	CHLORINE.	BROMINE.	CHLORINE.	BROMINE.	CHLORINE.
40°	40°	5·7115	2·4844	3·381	1·397
60	60	5·6809	2·4810	2·872	1·261
80	80	5·6503	2·4776	2·223	1·122
100	100	5·6197	2·4742	1·719	0·984
120	120	5·5891	2·4708	1·650	0·845
160	160	5·5279	2·4641	0·058	0·571
—	200	—	2·4572	—	0·290
—	240	—	2·4504	—	0·0

Schoop[2] has examined the relation of density to temperature and pressure in the cases of several ethereal salts, besides propyl formate (see Appendix IV.).

There is a general resemblance between the course of the variation of density × and that of a dissociation-change. If the temperature is constant the variation of the density appears to be a function of the pressure; if the pressure is constant the variation appears to be a function of the temperature. If pressure decreases or temperature increases, the density decreases at first slowly, then more rapidly, and then again more slowly.

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[1] Schoop, *Wied. Ann.* **12.** 550.

[2] *Loc. cit.*

168. Naumann[1] has made a series of experiments on the density of the vapour obtained by heating acetic acid at different temperatures and pressures. The following table gives a synopsis of his results.

DENSITY OF ACETIC ACID VAPOUR.

Density corresponding to formula $C_2H_4O_2 = 2{\cdot}08$ (air = 1). Boiling point = 119°.

Pressure.	Density at 110°.	Pressure.	Density at 120°.	Pressure.	Density at 130°.
411 mm.	3·31	432 mm.	3·14	455 mm.	2·97
359 „	3·22	377·5 „	3·06	398·5 „	2·89
197 „	2·91	252 „	2·94	274 „	2·68
166·5 „	2·81	209 „	2·75	221 „	2·61
138·5 „	2·78	180 „	2·61	201 „	2·56
98·5 „	2·61	149 „	2·60	188 „	2·50
84 „	2·49	106 „	2·46	157·5 „	2·47
		89·5 „	2·37	112·5 „	2·34
				93 „	2·32

Pressure.	Density at 140°.	Pressure.	Density at 150°.	Pressure.	Density at 185°.
477 mm.	2·82	498·5 mm.	2·68	565 mm.	2·36
417·5 „	2·75	436·5 „	2·63	495 „	2·31
287·5 „	2·54	300 „	2·44	382 „	2·25
232 „	2·50	243 „	2·40	335 „	2·23
199 „	2·40	208 „	2·29	269 „	2·22
168 „	2·32	175 „	2·26	230 „	2·14
117 „	2·27	103 „	2·16	191·5 „	2·13
98 „	2·24			110·5 „	2·11

169. These numbers present us with a change which is very analogous to an undoubted case of dissociation, e.g. dissociation of N_2O_4 or PCl_5.

The formula obtained by Willard Gibbs (see p. 130) very approximately represents the relations between the density, the temperature, and the pressure, in the case of acetic acid vapour, and also in those of nitrogen tetroxide and phosphorus pentachloride.

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[1] *Annalen*, **155**. 325.

If the decrease in the density of acetic acid vapour as temperature increases is regarded as due to the dissociation of more complex, into less complex, bodies, then we must suppose that at certain temperatures and pressures this vapour consists, for the most part, of molecules the mass of each of which is greater than that represented by the formula $C_2H_4O_2$. Now as, on this hypothesis, these molecules are continuously breaking up into simpler groups of atoms, until the gas consists of $C_2H_4O_2$ molecules, after which no further change occurs, it seems better not to apply the term molecule to the heavier groups, but rather to use some such expression as molecular group, or even particle.

The same argument might apply in the cases of gaseous dissociation already considered. It might be better to speak of N_2O_4, PCl_5, $C_5H_{11}Br$ &c. as molecular groups rather than as molecules.

170. A distinction of this kind has been drawn between compounds which readily separate into simpler constituents when heated, and compounds which are stable in the gaseous state throughout a considerable range of temperature; the names 'molecular compounds' and 'atomic compounds' being used to distinguish these classes of bodies.

The phenomena we have examined in this and preceding paragraphs seem to me to point to the existence of gaseous particles of varying degrees of complexity, and to shew that the more complex particles are as a rule not so stable, as regards rise of temperature or fall of pressure, as the less complex particles of the same elementary composition.

Facts oblige us, I think, to recognise various orders of small particles. Theory undoubtedly points in the same direction. Nevertheless it is impossible to say where the so-called 'atomic compounds' end and the 'molecular compounds' begin[1].

171. The dissociation of the gaseous molecules of an element into atoms has been studied in the case of iodine vapour. The results, which are presented in the following table, shew that this process is strictly analogous to the dissociation of nitrogen tetroxide.

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[1] This subject is more fully treated in the author's *Principles of Chemistry*, pp. 202—222.

DISSOCIATION OF IODINE VAPOUR[1].

(Density calculated for formula $I_2 = 8{\cdot}77$.)

Pressure.	Temp.	Density of vapour (air = 1).	Mean percentage dissociation per 100°.
760 mm.	448°	8·74	
	680	8·23	
	764	8·28	
	855	8·07	
	940	7·60	6·9
	1040	7·01	10·2
	(approx.) 1275	5·82	11·0
	1390	5·27	13·7
	1468	5·06	8·8

Pressure.	Temp.	Density of vapour (air = 1).	Mean percentage dissociation per 76 mm. decrease.
760 mm.	1250°	5·8	
304 „		5·54	1·2
228 „		5·30	7·1
152 „		5·07	7·5
76 „		4·72	13·7

A comparison of these results with those tabulated on p. 126 (par. 151) for nitrogen tetroxide shews that there is no difference of kind between the separation, by the agency of heat, of more complex into less complex compound molecules on the one hand, and of the elementary molecule I_2 into its constituent atoms $I + I$, on the other hand.

172. But as the amount of separation of a compound gas into its constituents by heat is in some cases nearly independent of pressure, so the amount of separation of the molecules of an elementary gas into simpler groups of atoms is also in some cases dependent on the pressure only within wide limits. Thus the density of sulphur vapour varies with the temperature, but at a low temperature it appears to be independent of the pressure[2].

Density of Sulphur Vapour (air = 1).

Pressure.	Temperature.					
	440°	520°	660°	860°	1040°	about 1400°
760 mm.		6·62	2·93	2·23	2·24	2·20
104 „	6·7					
60 „	6·3					

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[1] Naumann, *Ber.* **13.** 1050, using the numbers of Crafts and Meier *do. do.* 868: also Crafts and Meier, *Compt. rend.* **92.** 39.

[2] *Troost, Compt. rend.* **86.** 1396.

The density of ozone is also independent of pressure within certain limits of temperature.

For data bearing on the subjects discussed in sections II. and III. of this chapter see Appendix IV.

SECTION IV. *Solution and Hydration*[1].

173. The addition of water to a concentrated solution of a chemical compound sometimes brings about the separation of the compound into two or more constituents.

The amount of chemical change is frequently dependent on the relative masses of the water and the dissolved compound, and on the temperature. If the masses are kept constant the amount of chemical change, in some cases, increases as the temperature rises, and the original compound is re-formed on cooling.

A saturated aqueous solution of ammonium acetate loses ammonia when a current of hydrogen is passed through it even at 0°, hence the solution probably contains free ammonia, and, if so, also free acetic acid. An aqueous solution of ferric chloride undergoes partial separation into hydrochloric acid and a colloidal soluble form of ferric hydrate; the amount of separation increases as the dilution increases. An aqueous solution of ferric nitrate is also partially separated into its constituents; the amount of separation increases as the temperature increases, the quantity of water being kept constant[2]. Aqueous solutions of chromic sulphate, chrome alum, ammonia-iron alum, potash-iron alum, and some other alums, appear to undergo partial separation into their constituents when heated. Some of these solutions yield precipitates of basic salts at moderately high temperatures[3].

Analogies have been traced between such changes as these and processes of dissociation. But even the simplest case of so-called 'dissociation in solution' presents much more complex phenomena than a case of true dissociation. The action of water has been compared to that of pressure; dilution has been regarded as analogous to decreased pressure. In most of these so-called dissociations water is one of the constituents of the dissociating system; hence, judging from the supposed analogy, we should expect the process to become slower, and finally to stop, as the quantity of water increases. But the reverse of this actually occurs. The water probably exerts two actions; one, which may be called physical, whereby an increase in the quantity of water gives greater freedom of motion to the particles of the dissolved substance, and also lessens the chances of combination between the separated constituents of the substance; and another, which may be called chemical, whereby an increase in the quantity of water determines the formation or decomposition of definite compounds which would not otherwise be produced. While an increase in the quantity of water may, in one respect, tend to increase the amount of chemical change, it may, in the other respect, exert an influence in the opposite direction. When the physical is much more marked than the chemical action of water, we shall have phenomena resembling those presented in gaseous dissociation[1].

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[1] It is not proposed fully to discuss the phenomena of solution and hydration. We are interested in these occurrences here in so far as they are concerned with thermochemical changes.

[2] For details both of methods and results see G. Wiedemann, *Pogg. Ann.* **126.** 1: **135.** 177.

[3] See C. R. C. Tichborne, *Chem. News*, **24.** 202; 210. L. de Boisbaudran, *Compt. rend.* **79.** *1491.* And A. Naumann, *Ber.* **8.** 1630.

10—2

174. The first part of Thomsen's third volume is devoted to the consideration of solution in water, and hydration, of salts[2].

The *heat of solution* of a definite chemical substance is the total quantity of heat produced during the solution of a specified mass (generally one formula-weight) of that substance in a stated mass of water.

The *heat of dilution* of a solution is the total quantity of heat produced during the dilution, with a specified mass of water, of a stated mass of solution the composition of which is defined.

The *heat of hydration* of a compound is the total quantity of heat produced during the combination of a specified mass of the compound with liquid water, with production of a definite hydrated salt.

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[1] See Naumann's *Thermochemie*, 158—167; and article 'Dissociation' in *Neues Handwörterbuch der Chemie*, especially pp. 999—1002.

[2] The following pars. (174—195) are a condensed translation of Thomsen's book, vol. 3. pp. 3—216.

The initial temperature is always approximately 18° C.

175. The following are the more important conclusions which Thomsen draws from his experimental results[1].

I. *Heats of solution of dehydrated salts.*

(i) Those dehydrated salts which dissolve in water with evolution of heat also form crystallisable compounds with water, or they are completely decomposed by water. All salts which form crystallisable compounds with water do not however dissolve with evolution of heat.

(ii) Those salts which do not form crystallisable compounds with water, and are not completely decomposed by that liquid, dissolve in water with absorption of heat.

The first group comprises the dehydrated haloid compounds of Li, Ba, Sr, Ca, Mg, Al, Zn, Mn, Fe, Co, Ni, Cu, and Sn. To this group belong also $CdCl_2$ and $CdBr_2$, $AuCl_3$, and NaI; K_2CO_3; most of the salts of sodium, e.g. the sulphate, carbonate, phosphate, borate, &c.; and all the dehydrated salts of metals of the magnesium group.

The second group comprises the haloid compounds of K, Pb, Tl, Hg, and Ag; CdI_2 and $AuBr_3$; and the potassium-haloid compounds of Pt, Pd, and Hg.

To this group belong also most of the salts of potassium, e.g. the nitrate, sulphate, chlorate, dichromate &c.; and many salts of Pb, Tl, and Ag.

The two salts NaCl and NaBr belong to neither group; they dissolve in water with absorption of a small quantity of heat; thus,

$$[NaCl, Aq] = -1{,}180\,;\; [NaBr, Aq] = -190.$$

These salts therefore do not belong to Group I; they form crystallisable compounds with water and therefore do not belong to Group II.

II. *Heats of solution of hydrated salts.*

Most hydrated salts dissolve in water with absorption of heat. Some however dissolve with evolution of heat. Among the latter are $Li_2SO_4H_2O$, $BeSO_44H_2O$, $MnSO_45H_2O$; and the haloid salts $MgCl_26H_2O$, $MnCl_24H_2O$, $FeCl_24H_2O$, $CdCl_22H_2O$, and $CuCl_22H_2O$. Thomsen supposes that those hydrated salts which dissolve with evolution of heat are capable of forming hydrates containing more water than is contained in the salt before solution. Thus he supposes that the salts $MnCl_26H_2O$, $FeCl_26H_2O$, $CdCl_26H_2O$, &c. exist under certain conditions which have not yet been experimentally realised[1].

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[1] *Loc. cit.* 3. 204—216.

176. If the differences between the heats of solution of analogous salts are tabulated certain well-marked regularities become evident[2]. Thus,

R	$[R^2SO^4, Aq]-[R^2N^2O^6, Aq]$
K	10,660
Na	10,520
Tl	10,660
NH_4	10,270.

The difference has nearly a constant value.

Again let us compare the differences between the heats of solution of haloid salts of various pairs of chemically analogous metals:—

X	$[Na^2X^2, Aq]-[K^2X^2, Aq]$
Cl	6,520 = 2.3,260
Br	9,780 = 3.3,260
I	12,660 = 4.3,165
$Pt_{\frac{1}{2}}Cl_3$	22,300 = 7.3,186
$Pt_{\frac{1}{2}}Br_3$	22,250 = 7.3,179.

The differences are whole multiples of a constant, approximately equal to 3,200. This constant appears again in the following difference:—

$$[Li^2Cl^2, Aq]-[Na^2Cl^2, Aq] = 19,240 = 6.3,207.$$

The same constant is repeated in the following groups of differences:—

S	S′	[S, Aq] - [S′, Aq]
$MgCl_2$	$CaCl_2$	18,510 = 6.3,085
$CaCl_2$	$SrCl_2$	6,270 = 2.3,135
$SrCl_2$	$BaCl_2$	9,070 = 3.3,023.

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[1] *Loc. cit.* 3. 208—209.

[2] Id. *loc. cit.* 3. 211—213.

$CaCl_2 6H_2O$	$SrCl_2 6H_2O$	3,160 = 1.3,160
$CaBr_2 6H_2O$	$SrBr_2 6H_2O$	6,130 = 2.3,065.
$CuCl_2$	$BaCl_2$	9,010 = 3.3,003
$CuBr_2$	$BaBr_2$	3,270 = 1.3,270.
$CuCl_2 2H_2O$	$BaCl_2 2H_2O$	9,140 = 3.3,047
$CuCl_2 2H_2O$	$SnCl_2 2H_2O$	9,580 = 3.3,193.
$ZnCl_2$	$CdCl_2$	12,620 = 4.3,155
$ZnBr_2$	$CdBr_2$	14,590 = 4.3,645
ZnI_2	CdI_2	12,270 = 4.3,068.
Al_2Cl_6	Fe_2Cl_6	90,330 = 30.3,011
Fe_2Cl_6	Au_2Cl_6	54,460 = 18.3,025.

177. The following numbers shew that there are definite relations between the values of the heats of solution of various haloid salts and the atomic weights of the metals on the one hand, and of the halogens on the other[1]:—

	$X = Cl$	$X = Br$	$X = I$
$[BaX^2, Aq]$	2,070	4,980	—
$[SrX^2, Aq]$	11,140	16,110	—
$[CaX^2, Aq]$	17,410	24,510	27,690
$[MgX^2, Aq]$	35,920	—	—
$[Tl^2X^2, Aq]$	− 20,200	—	—
$[K^2X^2, Aq]$	− 8,880	− 10,160	− 10,220
$[Na^2X^2, Aq]$	− 2,360	− 380	+ 2,440
$[Li^2X^2, Aq]$	+ 16,880	—	—

The heat of solution of these analogous haloid salts is greater the greater the atomic weight of the halogen[2], and, the halogen being the same, the smaller the atomic weight of the metal.

	$X = Cl$	$X = Br$	$X = I$
$[ZnX^2, Aq]$	15,630	15,030	11,310
$[CuX^2, Aq]$	11,080	8,250	—
$[CdX^2, Aq]$	3,010	440	−960
$[PbX^2, Aq]$	− 6,800	− 10,040	—

In these cases the heat of solution is smaller the greater the atomic weight of the halogen, and, the halogen being the same, the greater the atomic weight of the metal[3].

The following chlorides exhibit heats of solution which increase as the atomic weight of the more positive element decreases; they are in this respect similar to the chlorides of the alkali and alkaline earth metals :—

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[1] Thomsen *loc. cit.* 3. 213—215.

[2] The potassium salts are exceptions to this statement.

[3] The *copper salts* form exceptions to this statement.

M	$[M^2Cl^6, Aq]$	M	$[MCl^4, Aq]$
Au	8,900	Sn	29,920
Sb	17,600	Ti	57,870
As	35,160	Si	69,260.
Fe	63,390		
P	130,280		
Al	153,690		

178. The difference between the heat of solution of a dehydrated salt and that of the same salt combined with a definite quantity of water represents the heat of hydration of the specified hydrate. Thus consider the following numbers :—

n	$[ZnSO^4nH^2O, Aq]$	*n*	Hence thermal value of the combination of the *n*th H_2O.	
0	18,434			
1	9,950	1	8,484	mean thermal value of each $H_2O=3,242$.
2	7,604	2	2,346	
3	5,258	3	2,346	
4	3,513	4	1,745	
5	1,335	5	2,178	
6	– 843	6	2,178	
7	–4,260	7	3,417	

179. Thomsen has examined about 40 salts in this way. The mean thermal value for the combination of one molecule (H_2O) of water[1] varies from 5,495 for $MgCl_2$ to 1,125 for $CdCl_2$.

The heat produced in a process of hydration wherein a solid hydrate is formed is due in part to the solidification of the water and in part to the chemical action which takes place. In every case examined by Thomsen, with the exception of cadmium chloride, the mean heat of hydration per molecule of water combined was greater than the heat of liquefaction of one molecule (H_2O) of water.

180. But when we look at the thermal values obtained for the combination of each molecule of water with the different salts we find that these values exhibit great variations. The process of hydration is evidently a complicated one.

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[1] That is the value of the reaction $\left[\frac{S, nH^2O}{n}\right]$ where S = dehydrated salt, and *n* = *maximum* number of water molecules which combine therewith.

Thomsen classifies the salts which he has examined in accordance with the number of water molecules which combine to form the highest hydrate. Let us consider the results thus obtained[1].

181. I. *Hydrated salts of the general form* $S.10H_2O$; *and* $S.12H_2O$.

(i) $Na_4P_2O_7.10H_2O$. This is the only salt examined in which the thermal value of the addition of each molecule of water is the same, viz. 2,352 units.

(ii) $Na_2HPO_4.12H_2O$. Sum of the thermal values of first and second molecules[2] of water = 6,030. Mean value of each molecule from third to twelfth (inclusive) = 2,244. Mean value for each molecule = 2,372. The process of hydration approaches that of $Na_4P_2O_7$ in the near equality of the thermal value of each molecule of water.

(iii) $Na_2SO_4.10H_2O$. Mean value per molecule of water = 1,922. Value of first molecule = 2,360; value of each of the following nine molecules = 1,873.

(iv) $Na_2CO_3.10H_2O$. The values of the various molecules of water shew great differences. The first has a larger value than any other, viz. 3,382; then follows the second = 2,234; then come six molecules arranged in three pairs the value of each pair being only very little different from that of any other, thus, third and fourth = 2 × 2,129, fifth and sixth = 2 × 2,076, seventh and eighth = 2 × 2,118. Finally the ninth and tenth molecules have smaller values than any of the others, viz. 2 × 1,764.

182. II. *Salts of the general form* $S.6H_2O$; $S.4H_2O$; *and* $S.2H_2O$.

The salts examined were these:—

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[1] *Loc. cit.* 3. 168—181.

[2] The expression 'thermal value (or sometimes simply value) of the first (or second &c.) molecule of water' will be used. The exact meaning of this phrase is 'the number of gram-units of heat produced during the formation of the hydrate $S.H_2O$ from the salt S and H_2O, or of the hydrate $S.2H_2O$ from the hydrate $S.H_2O$ and H_2O, or of the hydrate $S.3H_2O$ from the hydrate $S.2H_2O$ and H_2O, &c., where S = the formula-weight of the specified salt in grams, and H_2O = 18 grams of liquid water.' It should not be forgotten that a process or operation is connoted by the expression 'thermal value of a water molecule.'

$Na_2PtCl_6.6H_2O$
$K_2Mg(SO_4)_2.6H_2O$
$K_2Zn(SO_4)_2.6H_2O$
$K_2Cu(SO_4)_2.6H_2O$
$K_2Mn(SO_4)_2.4H_2O$
$SrCl_2.6H_2O$
$SrBr_2.6H_2O$
$CaCl_2.6H_2O$
$MgCl_2.6H_2O$
$BaCl_2.2H_2O$.

The hydration of the five double salts presents the phenomena summarised in the following table.

Thermal value of the combination of the n*th molecule of* H_2O.

n	Na_2PtCl_6	$K_2Mg(SO_4)_2$	$K Zn(SO_4)_2$	$K_2Cu(SO_4)_2$	$K_2Mn(SO_4)_2$
1 2	2.4,320	2.4,930	2.3,731	2.5,303	2.4,648
3 4	2.2,540	2.2,950	2.2,728	2.2,993	2.1,760
5 6	2.2,725	2.2,430	2.3,445	2.3,186	—
Sum	19,170	20,620	19,808	22,964	12,816.

The thermal phenomena accompanying the hydration of the chlorides belonging to this group are presented by Thomsen as follows :—

Thermal value of the combination of the n*th molecule of* H_2O.

n	$SrCl_2$	$SrBr_2$	$CaCl_2$	$BaCl_2$	$MgCl_2$
1	5,260	6,150	7,440	3,170	20,940
2	3,800	3,800		3,830	
3	2.2,460	2.3,100	14,310	—	2.4,370
4				—	
5	2.2,330	3,160		—	
6		4,020		—	3,290
Sum	18,640	23,330	21,750	7,000	32,970.

The hydration of the double salts in this group is characterised by great symmetry; the water molecules seem to be combined in three pairs, the thermal value of the first pair being much greater than that of the succeeding pairs. The haloid salts of this group do not exhibit this symmetry so fully as the double salts; the value of the first molecule of water is generally greater than that of the second.

183. III. *Salts of the general form* $S.7H_2O$ *; and* $S.5H_2O$.

The salts examined were $MgSO_4.7H_2O$, $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$, and $MnSO_4.5H_2O$. The results are these :—

Thermal value of the combination of the n*th molecule of* H_2O.

n	$MgSO_4$	$MnSO_4$	$ZnSO_4$	$CuSO_4$
1	6,980	5,990	8,480	6,460
2	2,300	1,600	2.2,346	2.3,250
3	2.3,400	2.1,980		
4			1,745	2,180
5	2.2,170	2,200	2.2,178	3,410
6		—		—
7	3,660	—	3,418	—
Sum	24,080	13,750	22,690	18,550.

Here we see that the value of the first molecule is much greater than that of any of those which succeed it. The value of the last molecule (in the case of $MgSO_4$ and $ZnSO_4$ the seventh, and in that of the other two salts the fifth) is greater than that of any other except the first. Each heptahydrated salt contains two pairs, and each pentahydrated salt one pair, of water molecules, the thermal value of the combination with the rest of the salt of each molecule in any of these pairs being equal to that of the other molecule in the same pair[1].

184. When an acid, an alkali, or a salt, is dissolved in water, is a hydrate, or a series of hydrates, produced? Does the evolution of heat during solution, or dilution, necessarily point to the formation of chemical compounds?

Such questions as these are considered by Thomsen in the first part of his third volume. The data accumulated represent the thermal values of the solution and dilution of 9 acids, 3 alkalis, and 35 salts[2].

Let us take one or two typical cases and treat them in some detail.

185. SULPHURIC ACID.

(i) *Heat of solution of the anhydride* SO_3.

m	$[SO^3, mH^2O]$	m	$[SO^3mH^2O, H^2O]$
0·5	12,010	0	21,320
1	21,320	1	6,379
2	27,699	2	3,039
3	30,738	3	1,719.
1600	39,165		

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[1] In connection with these results see Pickering, *C. S. Journal*, **Trans.** for **1884**. 686; and **1885**. 100.

[2] For an account of the experimental methods and the necessary calculations see Thomsen *loc. cit.* *3*. *39*—*43*.

These numbers shew that rather more than one-half of the heat produced by adding a practically infinite quantity of water to the anhydride SO_3 is produced by the addition of the first molecule of water; and also that the addition of the second molecule of water produces less than one-third of the quantity of heat produced by the addition of the first molecule. Hence there can be little doubt that the product of the mutual action of SO_3 and H_2O, in the proportion expressed by these formulæ, is a definite hydrate. This conclusion is confirmed by the preparation of the definite hydrate in question, viz. H_2SO_4.

(ii) *Heat of dilution of the liquid hydrate* H_2SO_4.

n	$[H^2SO^4, nH^2O]$	n	$[H^2SO^4, nH^2O]$
1	6,379	49	16,684
2	9,418	99	16,858
3	11,137	199	17,065
5	13,108	399	17,313
9	14,952	799	17,641
19	16,256	1599	17,857.

These numbers are thrown into the form of a curve in the 1. plate facing p. ~~158~~. The curve AB gives the thermal value of the addition of water up to 20 molecules, the abscissæ representing numbers of water-molecules and the ordinates gram-units of heat evolved. The heat of dilution for 20 to 200 molecules H_2O is shewn by the curve ab where the abscissæ are on a reduced scale. The curve shews no appearance of any irregularity which one would expect to find were a definite hydrate formed by dilution. The heat of dilution approaches a maximum and appears to be a hyperbolic function of the quantity of water. Such a function may be most simply expressed by the formula

$$y = \frac{nC}{n + r}$$

where C and r are two constants for which approximate values may be obtained. The following values for these constants are obtained from the first five numbers in the preceding table:—

$$C = 17{,}860$$
$$r = 1{\cdot}7983.$$

This formula may then be applied to calculate the value of the heat of dilution of sulphuric acid for different masses of water, Thus if y = heat of dilution for n H_2O we have

$$y = \frac{n \,.\, 17{,}860}{n + 1{\cdot}7983}.$$

The following table presents the calculated and observed results up to a dilution of 20 molecules H_2O :—

$[H^2SO^4, nH^2O]$

n	*observed*	*calculated*	*difference*
1	6,379	6,382	− 3
2	9,418	9,404	+ 14
3	11,137	11,167	− 30
5	13,108	13,135	− 27
9	14,952	14,886	+ 66
19	16,256	16,315	− 59
1599	17,857	17,840	+ 17.

When $n = \infty$ the formula gives the heat of dilution as 17,860 units, which is practically identical with the number obtained when $n = 1599$; nevertheless if the observed values for 50, 100, 200 &c. molecules H_2O are compared with the values calculated by the formula considerable differences are evident. Thus,

n	*observed*	*calculated*	*difference*
19	16,256	16,315	− 59
49	16,684	17,228	− 544
99	16,858	17,541	− 683
199	17,065	17,701	− 636
399	17,313	17,780	− 467
799	17,641	17,821	− 180
1599	17,857	17,840	+ 17.

Thomsen thinks that these differences are to be accounted for by the very probable supposition that the production of heat is the accompaniment of (1) the action of the water on the acid; and (2) the contraction in the volume of the liquid, whereby heat is produced in accordance with a law different from that which expresses the production of heat in the first action.

There can be little or no doubt however that these results point to the non-formation in aqueous solutions of SO_3 of definite hydrates, except that one the composition of which is expressed by the formula H_2SO_4.

186. NITRIC ACID.

The heat of dilution of the acid HNO_3 for one to five molecules H_2O agrees very closely with that calculated by means of the formula

$$y = \frac{n \cdot 8{,}974}{n + 1{\cdot}737}.$$

The constants 8,974 and 1·737 are obtained from experimental results.

The following table presents the observed and calculated values of the heat of dilution:—

$[HNO^3, nH^2O]$

n	*observed*	*calculated*	*difference*
0·5	2,005	2,008	− 3
1·0	3,285	3,285	0
1·5	4,160	4,160	0
2·0	—	4,808	—
2·5	5,276	5,301	−25
3	5,710	5,690	+20
4	—	6,266	—
5	6,665	6,668	− 3.

On further dilution the observed numbers are rather smaller than the calculated, but the value of the heat of dilution scarcely increases after the addition of five molecules H_2O. Thus for 20 molecules it is equal to 7,458, and for 320 molecules it is 7,493 units.

The foregoing results are represented graphically in the curve AC in the plate facing this page. The heat of dilution is a continuous function of the quantity of water added; there are no irregularities such as would point to the production of definite hydrates of HNO_3.

187. PHOSPHORIC ACID.

Thomsen's results are represented by the curve AD in the plate. This curve is analogous to those for the two acids already considered. There is no evidence of the formation of any definite hydrate of H_3PO_4.

The curve AE (plate facing this page) represents the heat of dilution of alcohol. This curve closely resembles the curves for the acids H_2SO_4, HNO_3, and H_3PO_4. There are certainly no hydrates formed when alcohol is diluted with water.

188. HYDROCHLORIC ACID.

The heat of dilution of a concentrated aqueous solution of hydrochloric acid, with a quantity of water varying from 2·62 to 200 molecules H_2O for each molecule HCl, follows the same law as that observed in the cases of sulphuric and nitric acids. Thomsen's results however point to the existence of a definite hydrate containing hydrochloric acid and water in the proportion $HCl . H_2O$.

The formula already given representing the heat of dilution of an acid as a continuous hyperbolic function of the quantity of water added, viz.

$$y = \frac{n \,.\, C}{n+r},$$

will assume the following form if an aqueous solution of an acid containing n molecules H_2O for each molecule acid is diluted with m molecules H_2O :—

$$y_{n+m} - y_n = \left(\frac{n+m}{n+m+r} - \frac{n}{n+r}\right) C = \left(\frac{r}{n+r} - \frac{r}{n+m+r}\right) C.$$

If m is made very large the heat of dilution will approximate to the value $\frac{rC}{n+r}$.

The experiments with hydrochloric acid shew that when m is very large the heat of dilution is nearly inversely proportional to the quantity of water originally present; that is to say, the heat of dilution of the acid $HCl . n'H_2O$ is equal to $\frac{C}{n'}$. The two expressions $\frac{rC}{n+r}$ and $\frac{C}{n'}$ become identical only when $n < n'$; that is when a portion of the water originally present, n', is regarded as present not in the form of water but in definite combination with HCl.

Now other experiments conducted by Thomsen[1] have established a considerable probability in favour of the hypothesis that an aqueous solution of hydrochloric acid contains the hydrate $HCl . H_2O$. Assuming the existence of this hydrate, it follows that $n = n' - 1$, and the two expressions $\frac{rC}{n+r}$ and

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[1] See *loc. cit.* 2. 430—444.

$\frac{C}{n'}$ become identical when the constant r is taken as equal to unity.

The experimental results give the value of the other constant C as 11,980. The heat of dilution of the acid $HCl\,.\,n'H_2O$ with m molecules H_2O is then expressed by the equation

$$y = \left(\frac{1}{n'} - \frac{1}{n'+m}\right) 11{,}980;$$

where $y = [HCl\,.\,n'H^2O,\ mH^2O]$.

The following table exhibits the observed and calculated values of y:—

$[HCl.n'H^2O,\ mH^2O.]$ (Temp. 15°—18°·5.)

n'	$n'+m$	y		*difference*
		observed	*calculated*	
2·618	51·1	4,285	4,343	−58
2·618	91·7	4,372	4,456	−84
2·672	56·6	4,272	4,271	+ 1
3·206	71·2	3,587	3,569	+18
3·206	61·3	3,545	3,541	+ 4
3·535	74·1	3,296	3,228	+68
3·535	85·6	3,320	3,249	+71
5·023	51·8	2,157	2,144	+13
5·023	49·7	2,153	2,154	− 1
10	50	925	956	−31
25	50	213	240	−27
50	100	116	120	− 4
50	200	196	180	+16.

The small differences between the observed and calculated values of the heat of dilution shew that the hypothesis that an aqueous solution of hydrochloric acid contains the hydrate $HCl\,.\,H_2O$ is very probable[1].

The formula given above for finding y would represent the heat of dilution of one molecule gaseous HCl with 300 H_2O as equal to 11,940; the value actually observed by Thomsen was 17,316 units. The difference, 5,376 units, represents the thermal value of the absorption of one molecule gaseous HCl by water with formation of the liquid hydrate $HCl\,.\,H_2O$.

The numbers obtained for the heats of dilution of HBr and HI point to the existence of the hydrates $HBr\,.\,H_2O$ and $HI\,.\,H_2O$ respectively.

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[1] For more details see Thomsen, *loc. cit.* **3.** 11—13; and 68—72.

189. ACETIC ACID.

The variation of the heat of dilution of pure $C_2H_4O_2$ with varying quantities of water shews great differences from the results observed in the four preceding cases. The following table presents Thomsen's results[1]:—

$[C^2H^4O^2 . n\, H^2O, \quad m\, H^2O]$

n	n + m									
	0·5	1	1·5	2	4	8	20	50	100	200
0	−130	−152	−165	−156	−111	− 2	+173	278	335	375
0·5		− 22	− 35	− 26	+ 19	+128	303	408	465	505
1			− 13	− 4	+ 41	150	325	430	487	527
1·5				+ 9	54	163	338	443	500	540
2					45	154	329	434	491	531
4						109	284	389	446	486
8							175	280	337	377
20								105	162	197
50									57	94
100										40

These results are represented graphically[2] in the curves on p. 162. *AB* shews the heat of dilution of $C_2H_4O_2$ with H_2O varying from 0·5 to 20 molecules; *A′B′* shews the heat of dilution with H_2O varying from 0·5 to 200 molecules, the abscissæ being 10 times smaller than in *AB*.

These results shew:

(1) That heat is absorbed on dilution of liquid $C_2H_4O_2$ with water until the amount of water added exceeds the proportion of $C_2H_4O_2 : 8H_2O$.

(2) That the maximum heat-absorption, viz. 165 units, occurs when the acid and water are mixed in the proportion of $C_2H_4O_2 : 1{\cdot}5H_2O$. When water is added to $C_2H_4O_2 . 1\frac{1}{2}H_2O$ heat is evolved.

(3) That heat is evolved when the quantity of water added exceeds the proportion $C_2H_4O_2 : 8H_2O$, and that the quantity of heat evolved increases regularly with increase of the water; when 200 H_2O is added to $C_2H_4O_2$ 375 units of heat are evolved.

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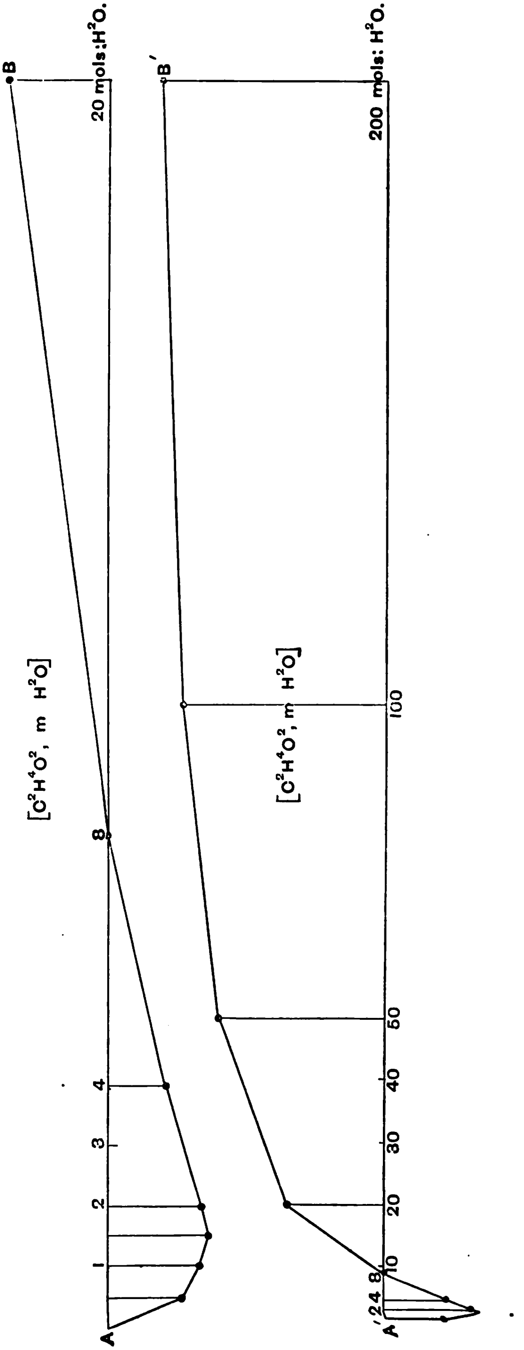
[1] *Loc. cit.* 3. 78.

[2] This and the preceding graphic representations are taken from Thomsen's *Untersuchungen*.


B
20 mols: H²O.
[C²H⁴O², m H²O]
8
4
3
2
1
A
B′
200 mols: H²O.
[C²H⁴O², m H²O]
100
50
40
30
20
10
8
4
2
A′

If a solution containing acetic acid and water in the proportion $C_2H_4O_2 : 1\frac{1}{2}H_2O$ is diluted to $C_2H_4O_2 . 200H_2O$, 540 units of heat are evolved; whereas if the liquid acid $C_2H_4O_2$ is itself diluted to $C_2H_4O_2 . 200H_2O$ only 375 thermal units are evolved.

Although the quantity of heat absorbed on dilution of $C_2H_4O_2$ reaches a maximum when $1\frac{1}{2}$ molecules of water are added, yet it is almost certain that no definite hydrate is formed having the composition $C_2H_4O_2 . 1\frac{1}{2}H_2O$. The heats of dilution of $C_2H_4O_2 . H_2O$ and $C_2H_4O_2 . 2H_2O$ are nearly the same as that of $C_2H_4O_2 . 1\frac{1}{2}H_2O$; further the quantity of heat absorbed on adding $\frac{1}{2}H_2O$ to $C_2H_4O_2$ is 130 units, whereas the quantity produced on addition of the second, third, and fourth $\frac{1}{2}H_2O$ is only -22, -13, and $+9$ units respectively, so that the total increase in the quantity of heat absorbed when the water increases from $\frac{1}{2}$ to $1\frac{1}{2}$ molecules is only 35 units.

When liquid acetic acid is diluted with water contraction occurs. The following numbers[1] shew that the amount of contraction increases as the quantity of water increases, and approaches a maximum of about 4·8 c.c.

Volume of $C_2H_4O_2$ grams $(20^0) = 57{\cdot}30$ c.c.; addition of xH_2O grams causes contraction of

$x = 0{\cdot}5$	1	2	3	4	8
1·52	2·26	3·11	3·59	3·97	4·27 c.c.

Now contraction of volume is accompanied by evolution of heat: but the contraction which occurs on addition of water to acetic acid is accompanied by absorption of heat until $8H_2O$ is added to $C_2H_4O_2$, and then by evolution of heat.

The contraction in the case of acetic acid is very nearly represented by the formula

$$c = \frac{n . 4{\cdot}8}{n + 1{\cdot}1}$$

where c = contraction, and n = number of molecules of H_2O added to one molecule of $C_2H_4O_2$. Now putting specific gravity = S, we have

$$S = \frac{\text{weight}}{\text{volume}};$$

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[1] v. Reiss, *Wied. Ann.* **10**. 295.

and in the case before us ($C_2H_4O_2 = 60$)

$$S = \frac{60 + 18n}{57{\cdot}30 + 18.1{\cdot}0018^1.n - \dfrac{n.4{\cdot}8}{n + 1{\cdot}1}}.$$

Hence the specific gravity of an aqueous solution of acetic acid is a complex function of n, that is of the number of molecules of water added to the acid. By differentiating, a maximum specific gravity is found when $n = 1{\cdot}02$, which agrees very well with the observed numbers. But this maximum is chiefly conditioned by the contraction, and not by the chemical composition, of the liquid. Hence, Thomsen concludes, the contraction of volume which occurs when acetic acid is diluted with water is a physical phenomenon and does not indicate the formation of any hydrate[2] of $C_2H_4O_2$.

190. FORMIC ACID, and TARTARIC ACID. There is no indication of the formation of hydrates in either case. The heat of dilution of formic acid is $+124$ for $\frac{1}{2}H_2O$, and $+172$ for H_2O. The heat of dilution of a solution of $C_4H_6O_6 . 6H_2O$ is a negative quantity[3], the value of which varies from $-3{,}240$ for $6H_2O$, to $-3{,}596$ for $200\ H_2O$.

191. Thomsen has studied the heats of dilution of the three alkaline solutions[4]

$$KOH . 3H_2O,\ NaOH . 3H_2O, \text{ and } NH_3 . 3H_2O.$$

The heat of dilution in each case is a positive quantity; that of $NH_3 . 3H_2O$ is very much smaller than that of $KOH . 3H_2O$ or $NaOH . 3H_2O$. There is no indication of the formation of a hydrate in any of these solutions[5].

192. When a dehydrated salt is dissolved in water and the solution is diluted it is possible that a hydrate (or hydrates) may be at first formed and then again separated into salt and water. The questions to be considered in examining the numbers representing the heats of solution and dilution of salts are thus two[6]:—

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[1] $1{\cdot}0018$ = vol. at 20^0 of 1 c.c. water taken at 4^0.

[2] See further Thomsen, *loc. cit.* **3.** 13—15; and 77—80.

[3] See for fuller details Thomsen, *loc. cit.* **3.** 15; and 80—82.

[4] The hydrates $KOH . 3H_2O$, and $NaOH . 3H_2O$ are chosen as starting points because these hydrates are liquid at ordinary temperatures.

[5] *Loc. cit.* **3.** 16; and 82—86.

[6] *Thomsen, loc. cit.* **3.** 20—34.

(i) Does a partial decomposition occur when a saline solution is diluted?

(ii) Does the aqueous solution of a specified salt contain definite compounds of that salt and water?

193. I do not propose to consider Thomsen's results in detail but rather to give a condensed translation of his conclusions (*loc. cit.* 3. 28—34).

We have already had before us Thomsen's classification of dehydrated salts in accordance with the positive or negative values of their heats of solution (see par. 175). Of the 35 salts, solutions of which Thomsen has examined with regard to their heats of dilution, 18 form crystallisable compounds with water[1], dissolve in water with evolution of heat, and exhibit positive heats of dilution. The 18 salts in question are these:—

$CaCl_2$, $MgCl_2$, $ZnCl_2$, $NiCl_2$, $CuCl_2$; $KC_2H_3O_2$, $NaC_2H_3O_2$, $(NH_4)C_2H_3O_2$, $Zn(C_2H_3O_2)_2$; MgN_2O_6, MnN_2O_6, ZnN_2O_6, CuN_2O_6; $NaHSO_4$, $MgSO_4$, $MnSO_4$, $ZnSO_4$, $CuSO_4$.

Of the remaining 17 salts examined, 11 dissolve in water with absorption of heat, exhibit negative heats of dilution, and do not form crystallisable compounds with water at the ordinary temperature. The salts are these:—

$NaCl$, $(NH_4)Cl$, KBr, KCN; $(NH_4)_2SO_4$; $(NH_4)HCO_3$; $NaNO_3$, $(NH_4)NO_3$, SrN_2O_6, PbN_2O_6; $(NH_4)_2C_4H_4O_6$.

There is evidently then a definite connection between the heat of solution of a dehydrated salt and the heat of dilution of an aqueous solution of the same salt.

194. The heats of dilution of the following four salts are negative, although these salts form crystallisable compounds with water and dissolve in water with evolution of heat:—K_2CO_3, Na_2CO_3, Na_2SO_4, NaI. Now when a salt forms a definite crystallisable hydrate, and also dissolves in water with evolution of much heat, Thomsen thinks there can be little doubt of the existence of a hydrate (or hydrates) of that salt in an aqueous solution of the salt. But we have scarcely any data for finding

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[1] Except $NaHSO_4$ which is decomposed by water, and $KC_2H_3O_2$ and $(NH_4)C_2H_3O_2$ which are very soluble in water at ordinary temperatures.

the composition of the hydrate or hydrates in such a solution[1]. Thomsen thinks it is probable that a salt in aqueous solution cannot combine with a greater number of molecules of water than are already combined with the acid and the base which by their union produce the salt. If this hypothesis is adopted the extent of hydration of a salt in aqueous solution must be conditioned by the nature both of the acid and the base. Hence it is quite possible that the constitution of dilute aqueous solutions of two salts may be different, although both form definite crystallisable compounds with water, and both dissolve in water with evolution of heat.

195. There yet remain two salts of the 35 examined by Thomsen, which exhibit negative heats of dilution, viz.

$KHSO_4$ and $(NH_4)HSO_4$.

But Thomsen has shewn that aqueous solutions of these salts, as well as of other acid sulphates, are decomposed by water, into neutral sulphate and free acid[2]. The heats of dilution of solutions of $KHSO_4$ and $(NH_4)HSO_4$ are doubtless complex functions of the heats of dilution of the constituents of these solutions, viz. K_2SO_4, or $(NH_4)_2SO_4$, and H_2SO_4.

196. Considering the whole of his investigation on the heats of solution and dilution of acids, alkalis, and salts, Thomsen says that the results he has obtained are altogether opposed to the supposition that aqueous solutions of these compounds contain various hydrates differing in composition according to the quantity of water present[3]. His results rather point to the hypothesis that when an acid, an alkali, or a salt, dissolves in water, either a hydrate is formed and dissolved as such, or the compound is dissolved without combination with water; and that an increase in the quantity of water does not affect the chemical composition of the solution. At the same time the dilution of concentrated solutions of salts, alkalis, and acids, is always accompanied by evolution or absorption of heat.

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[1] The necessary data would involve determinations of the specific gravities, specific heats, transpiration-coefficients, refractive energies, and other physical constants, of the solutions in question (Thomsen, **3.** 32).

[2] See *loc. cit.* **3.** 30: also **1.** 132—141.

[3] *Loc. cit.* **3.** 32.

The value of this thermal change always varies with variations in the quantity of water of dilution, and this variation, whether positive or negative, seems to have the character of a hyperbolic function of the quantity of water added.

The cause of the variations in the values of the heats of dilution is therefore probably one and the same for all the solutions examined.

Thomsen would find this common cause in changes of the states of motion of the particles of the solutions. When two liquids mix without any tendency to separation, it is suggested that such changes in the motions of the two kinds of particles occur as result in the formation of a homogeneous liquid, the particles of which are in equilibrium because the mean motions of the different kinds of particles are the same. But this mutual accommodation (*Accomodirung*) of the particles is accompanied by a transference of energy from one kind to the other. In these transferences of energy Thomsen finds the cause of the thermal changes, positive or negative, which always attend the dilution of aqueous solutions of acids, alkalis, or salts.

197. Whether the explanation suggested by Thomsen of the cause of the thermal changes which occur when water is added to saline solutions is or is not to be accepted must depend on the results of further investigations. The generally adopted 'hydrate theory' of solution can scarcely be expected to survive the dissemination of Thomsen's researches.

198. This theory has also of late been shewn to be untenable in a series of important papers on the nature of solution by W. W. J. Nicol[1]. A detailed consideration of the contents of these papers would lead us too far afield; we may however glance at a few of the points which have a definite connection with thermal chemistry.

The solution of a salt in water is usually (but not invariably) accompanied by contraction; in other words, the specific gravity of the solution is usually greater than that calculated from the known specific gravity of the solid salt and that of water. If it is assumed (as has been done) that this contraction occurs only in the water, we can calculate the quantity of heat which must be evolved by the operation, and we can then compare this with the observed thermal value of the solution of the salt. The following numbers are given by Favre and Valson[1]:—

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[1] *Proc. R.S.E.* **1881-82.** 819: *Phil. Mag.* (5) **15.** 91: *C. S. Journal*, **Trans.** for **1883.** 135: *Phil. Mag.* (5) **16.** 121; *do.* (5) **17.** 150; *do.* (5) **17.** 137; *do.* (5) **18.** 179; *do.* (5) **18.** 364: *Ber.* **17.** 492.

[S, Aq] S	Heat produced by contraction if this occurs only in the water.	Thermal value of the complete operation.
$SrBr_2 . 6H_2O$	31,820	− 6,220
$CuSO_4 . 5H_2O$	125,760	− 2,580
$SrN_2O_6 . 4H_2O$	63,640	− 12,830
$Na_2I_2 . 4H_2O$	66,670	− 14,770.

If we accept this interpretation of the contraction which usually occurs during solution, we must be prepared to modify our prevalent conceptions regarding solution, and the arguments bearing on the chemical composition of saline solutions which are founded on these conceptions. But Nicol has shewn that the total contraction observed in a saline solution increases as the quantity of salt in solution increases, but at the same time the amount of contraction produced by each successive formula-weight of salt added is less than that produced by the preceding formula-weight. Nicol's experiments also shew that when the solubility of a salt increases considerably as temperature increases the contraction on solution is less at high than at lower temperatures; but that contraction is nearly independent of temperature when solubility is also nearly independent of temperature. Now if a large portion of the total heat of solution of a salt is due to contraction of the water, the heat of solution should be less at high than at low temperatures when the contraction is less, and should be nearly independent of temperature when the solubility is independent of temperature. But Berthelot has found that the heat of solution of a salt is, as a rule, greater at high than at low temperatures[2]. Even when two saline solutions are mixed without the occurrence of chemical action,—e.g. solutions of potassium and sodium chlorides, or a concentrated solution of one of these salts with a less concentrated solution of the same salt,—contraction sometimes occurs unaccompanied by any thermal change[3].

[1] *Compt. rend.* **77.** 579; see also Naumann's *Thermochemie*, 353—6.

[2] *Ann. Chim. Phys.* (5). **4.** 28.

[3] See Nicol, *C. S. Journal*, **Trans. for 1883. 135.**

It is scarcely possible then to assign the total contraction noticed on solution to the water alone. It is much more likely that the contraction is due to the mutual actions of the particles of water and of salt. Nicol developes a theory of solution founded on this conception of mutual attractions between (1) water and water particles, (2) water and salt particles, and (3) salt and salt particles.

Now the attraction of salt particles for salt particles may be lessened by fusion; and we have already learned (*ante*, par. 131) that the quantity of heat absorbed on solution of a salt after fusion and rapid cooling is generally less than that absorbed when the salt is dissolved before fusion. In this case there is less mutual attraction between the particles of the salt after fusion than before; hence less work has to be done by the water in separating the particles; and hence there is less loss of energy to the system of water and salt.

Again the greater the quantity of salt in solution the smaller will be the result of the attraction of dissimilar particles (water and salt), and the greater the result of the attraction of similar particles (salt and salt); hence the amount of contraction produced by each successive particle of salt should be less than that produced by the preceding particle. Experiment confirms this anticipation. Once more if change of temperature largely modifies the solubility of the salt, it will also largely modify the results of the various attractions; in other words the contraction on dilution of salts whose solubility varies much with temperature will be largely affected by changes of temperature. This is confirmed by experimental results.

Any condition which increases the attraction of the water-particles for the salt-particles will increase the solubility of the salt; as the quantity of salt in solution increases, the attraction of salt-particles for salt-particles will increase; when these two attractions are balanced the solution will be saturated.

Increase of the quantity of water will increase the attraction of water-particles for salt-particles, and decrease the mutual attraction of salt-particles. But this change will be accompanied by changes of motion of the particles and hence by changes of energy. Hence dilution of a saline solution must be attended with some thermal change until so much water is present that addition of more has no sensible effect on the attractions of the different kinds of particles present.

199. The heat of hydration of a solid salt,—that is, the quantity of heat produced by the combination of a specified mass of water with the quantity of the salt expressed by its formula to produce a definite hydrated salt,—is evidently a complex function of the nature of the salt and the number of molecules of water combined (see pars. 179—183). No hydrated salt examined by Thomsen, with the single exception of $Na_4P_2O_7 . 10H_2O$, exhibited identical thermal values for the combination of each molecule of water.

The difference which is commonly expressed in the terms 'water of constitution' and 'water of crystallisation' is evidently a real difference, but, in so far as we may judge from thermochemical data, it is strictly a difference of degree and not of kind. What may be called water of constitution in one salt must be termed water of crystallisation in another. Like most expressions used in chemistry for marking off classes of phenomena, these terms have been employed in too absolute a manner. Does the difference implied in the terms in question continue when salts are dissolved in water? This question has been considered in pars. 184—196.

Thomsen has undoubtedly done a piece of most excellent work in his thermal study of the phenomena of solution and dilution. He has cleared away a number of false conceptions which have been very harmful in thermochemical speculations. It may be, as suggested by Nicol, that an aqueous solution of a hydrated salt does not, as a rule, contain the hydrate as such. At any rate Thomsen has proved that hydrates are not usually present in aqueous solutions of acids and salts; and moreover, and this is most important, that dilution of such solutions does not produce hydrates, nor does addition of water to a solution containing a hydrate tend to produce other hydrates.

Thomsen's investigations, like those of Nicol, establish the fact that large thermal changes may be the accompaniments of physical actions even in circumstances where we should at first sight interpret the thermal changes as indices of chemical actions.

Finally a study of the thermochemical researches summarised in the paragraphs of this section convinces us that in dilute aqueous solutions of acids, alkalis, and salts, the mutual attractions between this kind of particles and that, and the transferences of energy between the different kinds of particles, have resulted in the production of homogeneous liquids which are chemically comparable. Hence trustworthy conclusions regarding the mutual chemical actions of the constituents of such liquids may be drawn from measurements of the thermal changes which occur when the liquids are mixed. This conclusion has an important bearing on many thermochemical investigations, e.g. on Thomsen's investigation of the relative affinities of acids.

For data regarding solution, dilution, and hydration see Appendix V.

CHAPTER V.

CHEMICAL INTERPRETATION OF THERMAL DATA.

200. EVERY chemical reaction consists of two parts; a transformation of matter, and a transformation of energy. The transformation of energy is measured by the quantity of heat evolved or absorbed in the passage of the changing system from one definite state to another, provided the conditions are so arranged that all the energy entering or leaving the system shall enter or leave in the form of heat. The transformation of matter, so far as it is a chemical transformation, is measured, when we know the masses and composition of the constituents of the system in the initial state, and the masses and composition of the constituents of the system in the final state. But proceeding along with the chemical transformation there is usually, if not always, a physical change. The transformation of energy is the accompaniment of the total material change whether chemical or physical. It is generally difficult, and sometimes at present impossible, to separate the change of energy into two parts and say, this part belongs with the chemical change of matter, and that with the physical. And if this separation can be made, a difficulty yet remains. The greater number of the thermal values of chemical operations must, in the present state of science, be interpreted almost apart from any definite theory of the structure of matter. The properties of a material system are conditioned by certain variables of which chemical composition is one. Now in modern chemistry the expression 'chemical composition' means a great deal; it means much more than a statement of the masses of the elements in a specified mass of a compound. The only theory of chemical composition which

has been found of scientific value is that which regards any portion of a specified kind of matter as composed of small particles, each of which is itself a structure. Chemical composition as understood by this theory implies the conceptions of the molecule and the atom: a knowledge of the composition of a chemical compound means a knowledge of the nature, number, and relative arrangement, of the atoms in the molecule of that compound. By relative arrangement of the atoms in the molecule we mean, at present, two things:—

(1) The actual valency of each atom, that is, the number of atoms between which and each specified atom there is direct mutual action;

and

(2) The distribution of the interatomic reactions in the molecule.

These two things do not exhaust the connotation of the expression 'relative arrangement of atoms in the molecule' but they indicate, I think, all that has as yet been practically included in that expression.

But the theory of the grained structure of matter has been developed from the study of gaseous phenomena, and can be strictly applied in its present form only to gases. On the other hand the majority of the chemical reactions for which thermal values have been hitherto determined are reactions between liquids and solids or between liquids and liquids. For this reason, if for no other, these thermal data must be interpreted to a great extent in terms other than those of the molecular theory. There may be, and there probably will be, a theory of the structure of liquids and solids developed on lines similar to those of the molecular theory of gases; but this theory is in the future. If we now apply the conceptions of the molecule and molecular structure gained by the study of gases to explain the phenomena of liquids and solids we must be careful to do so only in a wide and general manner.

Let us then look at some of the thermal values of chemical reactions with the view of finding what general interpretation may be put upon them, or what light they throw on the study of chemical change.

SECTION I. *The 'law of maximum work'.*

201. The total thermal value of a specified chemical operation, as we have again and again seen, represents the sum of many thermal changes, some of which are probably positive and some probably negative. Moreover the total value is generally conditioned by the temperature at which the chemical operation takes place, and by the physical changes,—such as change of state from liquid to solid or *vice versa*, change of volume or of pressure &c.,—which generally, or we may almost say, which always, accompany a chemical change.

If then it is granted, on the one hand, that the quantity of heat lost, or gained, by a chemical system in passing from a specified initial state to a specified final state measures the quantity of energy lost or gained by the system, and if it is granted that the difference between these quantities of energy is an index of the relations of the properties of the system in the two states; it follows that thermal measurements must help us to understand chemical operations, because they must help us to regard these operations as the material accompaniments of definite gains or losses of energy.

But, on the other hand, if these gains or losses of energy are accompanied by changes or operations which we call physical, as well as by those we call chemical (and which we are especially desirous to study), it must be impossible to lay down any very precise generalisation regarding the connections between changes of energy and the purely chemical portions of operations, wherein the chemical and the physical are so interwoven.

202. But, as I take it, Berthelot has fallen into this mistake in his statement of the 'law of maximum work', which runs thus[1]:—

> "Every chemical change accomplished without the addition of energy from without tends to the formation of that body or system of bodies the production of which is accompanied by the evolution of the maximum quantity of heat."

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[1] *Méc. Chim.* **1.** xxix.

This 'law' is stated by Berthelot in a more rigid form as the 'theorem of the necessity of reactions', thus[1]:—

> "Every chemical change which can be accomplished without the aid of a preliminary action or the addition of energy from without the system, necessarily occurs if it is accompanied by disengagement of heat."

203. We at once inquire: what is 'a chemical change accomplished without the addition of energy from without the system'? Is such an occurrence possible? Most chemical changes are started by adding heat to the system; some only begin when the system is acted on by light or electricity. Can any chemical change be separated from accompanying physical changes? A considerable portion of the thermal change which occurs when an acid, alkali, or salt, dissolves in water is certainly due to physical processes, even when there may be a definite chemical action between the salt and the water.

204. It is sometimes urged against the 'law of maximum work' that a chemical change, the thermal value of which is a positive quantity, does not occur. But in most cases of this kind strict examination shews that the thermal value of the change in question has been determined by very indirect methods. Thus Thomsen gives the following data

$$[I^2, O^5] = 40{,}030 \text{ gram-units.}$$

Nevertheless iodine and oxygen do not combine to form I_2O_5 even when a mixture of iodine vapour and oxygen is passed over hot spongy platinum[2]. But the value assigned by Thomsen to the reaction in question is determined by indirect methods from measurements of many chemical operations, almost every one of which is accompanied by physical changes. The operation represented in symbols as $I_2 + O_5$ has not been realised; other operations have been carried out; some of these have been analysed into parts, and the collocation of symbols $I_2 + O_5 = I_2O_5$ has occurred in one of these parts; thermal values have been experimentally determined; and the deduction has been made that, if the reaction $I_2 + O_5 = I_2O_5$ occurred as a part of one of the operations in question it would be attended with evolution of heat. But chemistry is more than the manipulation of symbols; it deals with realities. The reaction $I_2 + O_5 = I_2O_5$ ought to occur, it is said, if the law of maximum work is generally applicable. Here is a chemical process which, were it to occur without the addition of energy from without, would be attended by disengagement of a great deal of heat. Therefore by the theorem of the necessity of reactions it ought to take place. But it does not. Therefore...?

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[1] *Loc. cit.*

[2] See Wehsarg, *Ber.* **17.** 2896.

But we must not interpret the law of maximum work too strictly.

The operation $I_2 + O_5 = I_2O_5$ perhaps occurs as part of a cycle of changes; separate it from the changes which precede and from those which follow, and it does not occur. After all then it is not one of those reactions which proceed 'without the aid of a preliminary action;' and therefore, although its occurrence would involve disengagement of heat, it is not necessary that it should occur.

205. Moreover there are actions which actually take place although their calorimetrically determined value is a negative quantity. For instance, aqueous solutions of sulphuric acid and sodium sulphate react with production of sodium hydrogen sulphate and absorption of heat; a dilute solution of sodium acetate is decomposed by a solution of tartaric acid with absorption of heat; an acid with a small heat of neutralisation often removes a base from its combination with an acid having a large heat of neutralisation, thus the heat of neutralisation of hydrofluoric acid is very large (32,500), but its relative affinity is extremely small (5 when $HNO_3 = 100$). The strict upholders of the law of maximum work assert that in these reactions double compounds of uncertain composition are formed, or hydrates are produced and are again decomposed, or portions of the reacting acids or salts are present in the solutions as hydrates and portions as dehydrated compounds. By dexterously adding on a heat of hydration here, and subtracting a heat of dilution there, they make the thermal value of the operation appear as a positive quantity. When a chemical change is actually accomplished, and the total thermal value as determined by experiment is negative, then more *ingenious methods* of argument must be adopted. But most of the

reactions which are stated to occur with absorption of heat take place under conditions such that it is impossible to produce the compounds formed and exhibit them apart from the whole changing system. Hence it is possible in such cases that the representation given of the chemical operation may not be a true representation, and that the calorimetric determination does not measure the thermal change which really accompanies the specified chemical change. Thomsen's work on solution and dilution has removed or rendered valueless many of the favourite arguments of this kind of the followers of Berthelot[1].

206. Thirty years ago Thomsen[2] stated the 'law of maximum work' in this form:

> "Every simple or complex reaction of a purely chemical kind is accompanied by evolution of heat."

Let us see what this means. If we try to define the expression 'a reaction of a purely chemical kind', the only possible definition seems to me to be one in terms of the molecular theory. Thomsen himself tells us[3] that a reaction of a purely chemical kind is one which "proceeds without the expenditure of external energy and is accomplished only through the striving of the atoms towards more stable equilibrium." But can we separate the strivings of atoms from the mutual interactions of molecules? The definition does not help us much because we cannot apply it to actual chemical reactions. We want practical definitions in science.

207. Thomsen explains more fully his conceptions of chemical stability[4]. The occurrence of a chemical reaction, as also the nature of the products, and the conditions under which the reaction proceeds, depend chiefly, according to Thomsen, on (i) the striving of the atoms of the reacting bodies towards stable equilibrium, (ii) the resistance of the molecules to decomposition, and (iii) the stability of the possible products at the temperature produced by the reaction. We may say that the greater the molecular mobility and the atomic mobility of a given chemical system the more ready will that system be to undergo

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[1] See *ante*, pars. 196 and 199.

[2] See *Thermochemische Untersuchungen*, 1. 12—16.

[3] *Loc. cit.* 1. 16.

[4] Loc. cit. 2. 468—474.

change, and the less the molecular and atomic mobilities the more stable the system. In every purely chemical reaction these two will tend towards a minimum. The reduction of molecular and atomic mobility will be attended by evolution of heat.

This explanation, I think, explains away the value of the definition of the purely chemical reaction. The 'striving of the atoms' is only one of the factors which condition the chemical occurrence. Of the several possible states which the system may assume it does not follow that that one will be assumed, the passage to which, from the initial state, is attended by the greatest loss of energy. When the system has passed into state *a* it may remain unchanged, although the passage to state *b* would involve loss of energy, because under the given conditions state *a* is more chemically stable than state *b*. Thus consider the chemical processes,

(1) $6KOHAq+6Cl=3KClO+3KCl+3H_2O$; heat evolution= 76,200.
(2) $6KOHAq+6Cl=KClO_3+5KCl+3H_2O$; ,, ,, = 94,200.
(3) $6KOHAq+6Cl=6KCl+3H_2O+O_3$; ,, ,, =105,200.

When chlorine is passed into an aqueous solution of potash at the ordinary temperature reaction (1) occurs, although the occurrence of (2) or (3) would be attended with a much greater loss of energy to the system than reaction (1). But reaction (1) involves a less change of *chemical type* than either of the other reactions.

In other words the occurrence of one of several possible reactions is conditioned by the chemical relations of the products of the change to the original bodies, as well as by the greater or less running down of energy which accompanies each of the possible reactions.

208. The laws of energy must hold good in chemical processes as well as in physical. No chemical change involving a raising of energy from a less available to a more available form can occur without the degradation of an equivalent quantity of energy; but it does not follow that because a chemical change would be accompanied by a degradation of energy, that change *necessarily* occurs: "Otherwise the existence of explosives like

gunpowder would be impossible[1]." Indeed one may almost say, otherwise there would be no chemistry. All possible chemical systems would have run downhill by this time and there would be no means for bringing them up again. The majority of chemical changes are not suitable for the application of thermodynamic principles, inasmuch as only a few chemical operations are reversible. The attempt made by Berthelot to apply the conception of the degradation of energy to all chemical changes has not been successful.

209. The so-called law of maximum work has assumed various forms in thermal chemistry. Sometimes it is said that a chemical operation always proceeds so as to 'satisfy the stronger affinities' which come into play. What then are these 'stronger affinities'? Is the phrase 'satisfaction of the stronger affinities' only another way of saying that the operation will proceed in the direction which ensures the maximum running down of energy? Or is the expression synonymous with 'stronger mutual atomic attractions'?

If the second of these questions is answered in the affirmative, then consider a simple case[2]. A molecule AB is decomposed by heat, and the atom A then combines with another atom C to form the new molecule AC. The thermal change which occurs is represented by the expression

$$[A, C] - [A, B].$$

But the only connection between the two changes is that one furnishes the materials for the other. The second change begins (theoretically) when the molecule AB has been separated into A and B; hence the formation of AC will proceed whether[3]

$$[A, C] > [A, B], \text{ or } [A, B] > [A, C].$$

Even if 'the satisfaction of the stronger affinities' means only that heat is evolved, it may be asked why not a trace of water is produced when a mixture of two volumes of hydrogen, two of chlorine, and one of oxygen, is exposed to sunlight; although

$$[H^2, O] = 68{,}000, \text{ and } 2[H, Cl] = 44{,}000.^{4}$$

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[1] See Lord Rayleigh "On the dissipation of energy." *Proc. R. S.* March 5, 1875.

[2] L. Meyer, *Die modernen Theorien der Chemie*, 447—8 (4th Ed.).

[3] See *post*, pars. 222, 223.

[4] K. Bötsch, *Annalen*, **210**. 207.

Why is no water formed even if an electric spark is passed through a mixture of the same gases, as long as there is chlorine sufficient to combine with all the hydrogen[1]? Why, it may finally be asked, may a chemical reaction between two gases be prevented by expanding the gases, although as much heat would be evolved by the combination of the expanded gases as by that of the same gases when more condensed?

210. If then we interpret the law of maximum work vaguely, making it as wide as possible, it is opposed by many facts. Chemical reactions frequently occur involving absorption of heat; and of two or more possible reactions that one which is accompanied by the evolution of most heat does not always occur in preference to one of the others. If we define the law accurately, and confine it to 'purely chemical reactions', the practical applicability of it almost disappears. Such an operation as a purely chemical reaction is practically unknown.

211. But it may be asked: must all the energy which is lost by a changing chemical system during a definite operation make its appearance in the form of heat?

212. Energy appears in chemical operations in forms other than that of heat. Electrical energy, for instance, is produced during the chemical changes which occur in the battery, and in this case a large quantity of work may be done without any marked evolution of heat. We must distinguish, in chemical processes, between that part of the chemical energy which is freely changeable into other forms, and that which can leave the system only in the form of heat.

213. Helmholtz has considered this subject of the changes of chemical energy into other forms of energy[2]. That part of the chemical energy of a specified system which is freely changeable into other forms is called by Helmholtz the *free energy* (*freie Energie*), that which can leave the system only in the form of heat is called by him the *bound energy* (*gebundene Energie*). The total energy of the system is equal to the sum of these two. That a system should undergo change without the aid of external

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[1] K. Bötsch, *Annalen*, **210.** 207. See also Schlegel, *Annalen*, **226.** 133.

[2] "Die Thermodynamik chemischer Vorgänge," *Sitzber. der Wiss. Akad. zu Berlin*, **1882**; see *Wissenschaftliche Abhandlungen*, **2.** 958.

energy there must be an increase of the bound energy and a decrease of the free energy of that system. Hence a chemical reaction occurring in an isolated system will proceed in that direction which involves a change of free chemical energy into some other form of energy which is not necessarily the form of heat. The loss of energy measured by the quantity of heat produced during such a chemical process will not represent the total loss of energy of the system. A certain reaction may be attended by a greater evolution of heat than accompanies another reaction, and nevertheless there may be a greater running down of chemical energy in the second reaction than in the first.

The free energy of a system can be calculated only in completely reversible changes.

In most chemical operations, which are neither isothermal nor adiabatic, external work is done at the cost of the free energy, and heat is produced at the cost of the bound energy of the system. An increase of the temperature of the system denotes a change of free into bound energy; this bound energy may then be converted, by friction &c., either wholly or in part into heat. In such a case the quantity of heat produced during the passage of the system from its initial to its final state represents the difference between the total internal energies of the system in the two states. It is this difference which is measured in thermo-chemical investigations; but the work done by the free energy of the system, the free work (*freie Arbeit*), which determines the direction of the chemical change, is different from this, and cannot be measured by merely finding the total quantity of heat produced during the operation.

214. If we admit Helmholtz's conception of free and bound energy, and assent to his treatment of the relations between these and chemical change, it follows that the direction of a chemical operation cannot be predicted from a knowledge of the thermal values of the possible changes which may occur in the specified system. Thus when two acids react on a base, in dilute aqueous solution, and in equivalent quantities, the base is shared between the acids, not in the proportion calculated from the heats of neutralisation, but in that determined by the relative affinities of the acids.

The mere fact that the thermal value of a chemical operation, deduced from measurements of a series of changes of which the specified operation forms a part, is represented by a positive quantity, does not justify us in saying that this change or operation will occur if it is isolated from the cycle of change of which it forms a part. Hydrogen does not reduce an aqueous solution of potassium chlorate; but if a few pieces of zinc and a little dilute sulphuric acid are placed in the solution potassium chloride and water are at once formed. In the latter system there is probably an overplus of chemical energy, which, aided by the configuration of the particles of hydrogen accompanying this excess of energy, brings about the reduction of the chlorate to chloride of potassium. Many chemical processes which occur as parts of a larger cycle of change are probably accomplished by aid of the energy produced in the operations which form other parts of the cycle; if the specified process is cut off from the others which supply the required energy the conditions necessary for the occurrence of the process are removed[1]. These conditions cannot in many cases be restored by adding heat; energy in a form other than heat is required, and this form of energy can only be supplied by making the special operation one part of a cycle of changes.

Under one set of conditions there may be only a small supply of energy, but that energy is in a form wholly available for performing the required work; under another set of conditions there may be a large supply of energy, but that in a form wholly or in great part unavailable for the work which is to be done[2].

215. But although the 'law of maximum work' is found wanting whether we examine it from the practical or the theoretical point of view, nevertheless the fact remains that, when the physical conditions of comparable chemical processes are kept as nearly as possible constant, the process which involves the maximum production of heat very frequently

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[1] Compare "Chemical Equilibrium the result of the Dissipation of Energy," by G. D. Liveing (1885); especially Chaps. IV. and V.

[2] The researches of Willard Gibbs (see *ante*, par. 153) seem to justify the ertion that a gaseous system, even when chemical action is possible, will ys tend to settle down in that state in which the energy is at a minimum istent with the given entropy and volume, or in which the entropy is at a mum consistent with the given energy and volume.

occurs in preference to the other possible processes, or occurs to a considerably greater extent than any of these other processes.

Let us look at some classes of chemical processes from this point of view. We shall regard the quantities of heat produced in the different operations as giving relative measurements of the losses of energy which attend these operations.

216. *Precipitation of metals as sulphides from aqueous solutions by the action of an aqueous solution of sulphuretted hydrogen.*

The data are presented in the following tables[1].

TABLE I.

		Base.						
Reaction		CdO	PbO	CuO	HgO	Tl_2O	Cu_2O	Ag_2O
[Base 2HClAq, H^2SAq]	(1)	27,300	29,200	31,700	45,300	38,500	38,500	58,500
[Base Aq, 2HCl Aq][2]	(2)	20,300	15,400	15,300	19,000	27,500	14,700	42,600
difference [(1)-(2)] =		+7,000	13,800	16,400	26,300	11,000	23,800	15,900.

TABLE II.

		Base.						
Reaction		CdO	PbO	CuO	HgO	Tl_2O	Cu_2O	Ag_2O
[Base, H^2S]	(1)	32,100	34,000	36,500	50,000	43,300	43,300	63,300
[Base, 2HCl]	(2)	55,000	50,000	50,000	53,500	62,200	49,300	77,200
difference [(1)-(2)] =		−22,900	16,000	13,500	3,500	18,900	6,000	13,900.

TABLE III.

		Base.				
Reaction		$MnO.H_2O$	$FeO.H_2O$	$NiO.H_2O$	$CoO.H_2O$	$ZnO.H_2O$
[Base 2HCl Aq, H^2SAq]	(1)	10,700	14,600	18,600	17,400	18,600
[Base Aq, 2HCl Aq][2]	(2)	23,000	21,400	22,600	21,100	20,300
difference [(1)-(2)] =		−12,300	6,800	4,000	3,700	1,700.

To illustrate the application of these data take the case of cadmium. Thus,

$$[\mathrm{CdO\ 2HClAq,\ H^2SAq}] - [\mathrm{CdOAq,\ 2HClAq}] = 7{,}000.$$

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[1] See Naumann's *Thermochemie*, 505—510.

[2] Objection may be taken to some of these values on the ground that aqueous solutions of many of these bases are unknown (compare ante, pars. 99 and 118).

If an aqueous solution of the base CdO were mixed with equivalent quantities of HCl and H_2S, either $CdCl_2$ or CdS might be produced; the production of the latter would be accompanied by the evolution of 7000 gram-units of heat more than would attend the production of the former compound. But

$$[CdO, 2HCl] - [CdO, H^2S] = 22,900.$$

If the solid base CdO were acted on by equivalent quantities of gaseous HCl and H_2S, either $CdCl_2$ or CdS might be produced; the production of the former would be accompanied by the evolution of 22,900 gram-units of heat more than would attend the production of the latter compound.

Now we know that aqueous sulphuretted hydrogen precipitates cadmium sulphide from a solution of the chloride of this metal, and that gaseous hydrochloric acid decomposes solid cadmium sulphide with production of cadmium chloride. But we also know that if equivalent quantities of cadmium chloride, in solution, and sulphuretted hydrogen are mixed, only a small quantity of the former salt is decomposed; if we desire to precipitate all the cadmium as sulphide we must add a very large quantity of sulphuretted hydrogen. The same remark holds good for the mutual action of solid cadmium oxide and hydrochloric acid; more than one equivalent of the latter acid (as gas) must react on each equivalent of cadmium oxide if the whole of this base is to be converted into cadmium chloride.

The numbers

$$[2HCl, Aq] = 34,600, \text{ and } [H^2S, Aq] = 4,800$$

shew, that an aqueous solution of hydrochloric acid possesses much less energy than the same mass of hydrochloric acid in the form of gas, but that the difference between the quantities of energy in a specified mass of gaseous sulphuretted hydrogen and the same mass of the acid dissolved in much water is very much less than the corresponding difference in the case of hydrochloric acid. Moreover the greater the concentration of aqueous hydrochloric acid the less is the quantity of heat evolved on adding the gaseous acid to the solution; in other words a concentrated aqueous solution of hydrochloric acid contains much more energy than a dilute solution of the same mass of the same compound. Hence, although aqueous sulphuretted hydrogen precipitates cadmium sulphide from an aqueous solution of the chloride, nevertheless cadmium sulphide ought to be decomposed by a concentrated solution of hydrochloric acid. This conclusion is confirmed by the results of experiment.

The case of antimony is especially interesting. Antimony sulphide is decomposed by aqueous hydrochloric acid of greater concentration than $HCl . 6H_2O$; but if more water than this is present antimony chloride is decomposed by aqueous sulphuretted hydrogen. Hence the two reactions

$$\left\{\begin{array}{l} Sb_2S_3 + xHClAq = 2SbCl_3Aq + 3H_2SAq + (x-6)\,HCl, \\ 2SbCl_3Aq + xH_2SAq = Sb_2S_3 + 6HClAq + (x-3)\,H_2S \end{array}\right\}$$

may occur until equilibrium is established. This state of equilibrium will be conditioned by the relative energies of the reacting bodies, and this again by the relative masses of these bodies when the temperature is constant throughout the operation.

217. *Mutual actions of mercuric oxide, hydrochloric and hydrocyanic acids.*

The following data are taken from Naumann's book[1]:—

$[HgO, 2HCNAq] = 31{,}000$: products of the action are

$$Hg(CN)_2\,Aq + H_2O;$$

$[HgO, 2HClAq] = 18{,}900$: products of the action are

$$HgCl_2\,Aq + H_2O.$$

Therefore

$$\begin{aligned}[HgCl^2Aq, 2HCNAq] &= 31{,}000 - 18{,}900 \\ &= 12{,}100 : \text{ products being} \\ &\quad Hg(CN)_2Aq + 2HClAq.\end{aligned}$$

If the heat of solution of mercuric chloride is added to the number 12,100 we get the theoretical thermal value of the action of equivalent quantities of solid mercuric chloride and aqueous hydrocyanic acid: thus,

$[HgCl^2, Aq] = -3{,}300$: therefore

$$[HgCl^2, 2HCNAq] = 12{,}100 + (-3{,}300) = 8{,}800.$$

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[1] *Loc. cit.* 499—501.

But, on the other hand, consider the numbers,

$[HgO, 2HClAq] = 18,900$; but $[2HCl, Aq] = 34,600$; and $[HgCl^2, Aq] = -3,300$.

Now if solid HgO were acted on by gaseous 2HCl, and if solid $HgCl_2$ were thus produced, the theoretical thermal value of the action would be

$$[HgO, 2HCl] = 18,900 + 34,600 - (-3,300)$$
$$= 56,800.$$

Then consider the action of gaseous 2HCN on solid HgO,

$[HgO, 2HCNAq] = 31,000$: but $[2HCN, Aq] = 12,200$: and $[Hg(CN)^2, Aq] = -3,000$.

If then solid HgO were acted on by gaseous 2HCN, and if solid $Hg(CN)_2$ were thus produced, the theoretical thermal value of the action would be

$$[HgO, 2HCN] = 31,000 + 12,200 - (-3,000)$$
$$= 46,200.$$

From this value and that already obtained for the action of gaseous 2HCl on solid HgO it follows that

$$[Hg(CN)^2, 2HCl] = 56,800 - 46,200$$
$$= 10,600;$$

because, if we start with the system $HgO + 2HCl$ and from this produce the system $HgCl_2 + H_2O$ 56,800 thermal units are evolved, and if we start with the system $HgO + 2HCN$ and produce $Hg(CN)_2 + H_2O$ 46,200 thermal units are evolved; therefore if we start with the system $Hg(CN)_2 + 2HCl$ and from this produce the system $HgCl_2 + 2HCN$ the quantity of heat evolved must be represented by the difference 56,800 − 46,200, i.e. by the number 10,600.

The conclusions which may be drawn from these data are:—

(i) An aqueous solution of mercuric chloride will be decomposed by an aqueous solution of an equivalent quantity of hydrocyanic acid;

(ii) Solid mercuric chloride will be decomposed, but probably only to a partial extent, by an equivalent quantity of hydrocyanic acid in aqueous solution;

(iii) Solid mercuric cyanide will be decomposed, to some extent, by an equivalent quantity of gaseous hydrochloric acid, but not by this acid when in aqueous solution.

These conclusions are on the whole confirmed by experiment.

218. *Mutual action of sulphuretted hydrogen and iodine contrasted with that of the same acid and bromine*[1].

Iodine and sulphuretted hydrogen do not mutually react whether the iodine is present as a solid or as a gas, or is dissolved in carbon disulphide. But aqueous solutions of sulphuretted hydrogen and iodine at once react with production of an aqueous solution of hydriodic acid, and sulphur. The thermal values are these:—

$$[2H^2S, 2I^2] = 4[H, I] - 2[H^2, S] = -34{,}000;$$

this action does not occur;

$$[2H^2SAq, 2I^2Aq] = 4[H, I, Aq] - 2[H^2, S, Aq] = +34{,}400;$$

this action takes place rapidly.

These values have been determined,

$$4[H, I, Aq] = 52{,}800; \; 2[H^2, S, Aq] = 18{,}400.$$

The thermal value of the decomposition of $2H_2SAq$ by $2I_2Aq$ is made up of two parts; in one 52,800 gram-units of heat are evolved, and in the other 18,400 units are absorbed. Now were the (positive) value of the first of these parts to fall below about 18,000 units we should expect the decomposition to cease. An analysis of the reaction $4[H, I, Aq]$ shews that it is composed of two parts; (1) the heat of formation of 4HI, and (2) the heat of solution of 4HI: the values of these parts are as follows:—

$$4[H, I] = -24{,}800; \; [4HI, Aq] = 77{,}600;$$
$$\therefore 4[H, I, Aq] = 52{,}800.$$

Now if a given mass of hydriodic acid is added to a quantity of water already containing hydriodic acid in solution less heat is evolved than when an equal mass of hydriodic acid is added to pure water. The more concentrated the solution of the acid the smaller is the quantity of heat evolved on adding a specified mass of the acid. Should the value of the reaction [4HI, Aq] become less than + 43,000 then the value of the reaction 4[H, I, Aq] will become less than + 18,000; and under these conditions, as we have seen, the total value of the reaction [$2H^2SAq$, $2I^2Aq$] will become equal to zero.

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[1] Naumann, *Ber.* **2.** 177; **99.** 1574; (or *Thermochemie*, 502—505).

Hence the conclusion follows that the decomposition of aqueous sulphuretted hydrogen by aqueous iodine, the two being mixed in equivalent quantities, will proceed more slowly as the solution becomes charged with hydriodic acid, and after a time will probably cease.

Experiment shews that [4HI, Aq] $< 43,000$ when the solution of hydriodic acid acquires the relative density of 1·56 at 15°—20°. Experiment also shews that when this concentration is reached as a result of the mutual action of aqueous $2H_2S$ and $2I_2$ the action stops. But the change in question again proceeds if water is added so as to reduce the density of the solution of hydriodic acid, because the value of the reaction [4HI, Aq] then again becomes greater than 43,000. But a considerably more concentrated solution of hydriodic acid in water can be obtained than that whose density is 1·56. If such a solution, e.g. a solution boiling at 127° (pressure = 760 mm.) and having a density of 1·67, is shaken with flowers of sulphur the hydriodic acid is decomposed, with production of sulphuretted hydrogen and iodine, until the density of the solution becomes about 1·56 when the process stops.

The system consisting of hydriodic acid, sulphuretted hydrogen, iodine, sulphur, and water is under certain conditions in thermal and chemical equilibrium; this equilibrium is disturbed by altering the relative masses of the constituents of the system, because the alteration is accompanied by changes of the energies of these constituents.

The action of bromine on sulphuretted hydrogen is thermally very different from that of iodine.

$$[2H^2S,\ 2Br^2] = 4[H,\ Br] - 2[H^2,\ S] = +25,000.$$

Gaseous bromine readily decomposes gaseous sulphuretted hydrogen. If the substances react in solution the heat of solution of 4HBr (about 80,000 units) is added to the heat developed when they react as gases; when the solution of hydrobromic acid becomes so concentrated that no heat is evolved by the addition of more acid, the decomposition of the sulphuretted hydrogen still proceeds and the hydrobromic acid produced is evolved as gas.

219. We have already had other examples of the classification of comparable reactions in accordance with their thermal values. In Chap. IV. pars. 117—123 we considered the action of metals on water and on various acids; and we found that, from a knowledge of these values it is often possible to tell whether a specified metal will or will not decompose water or an aqueous solution of a given acid. But these examples also illustrate the shortcomings of the thermal method of predicting the occurrence, or the results, of chemical processes.

To say that a certain action would be attended by the evolution of more heat than another reaction between the same bodies is not to prove conclusively that the specified reaction will occur. We must know more about the chemical habitudes of the reacting bodies and the possible products of the reaction than is told us by thermal data only.

We have also seen that thermal data tend to obscure the importance of considering the masses of the acting bodies. One action may have a rather smaller positive thermal value than another and nevertheless the first action may proceed rather than the second if the mass of one of the reacting bodies is largely increased. To say that every chemical change is conditioned only by the quantity of heat produced in that change is to ignore all that has been done in recent years on the influence of mass in chemical operations. It is to go back to the time of Bergmann, only substituting tables of thermal data for the tables of affinity which were then in vogue.

We cannot be too often reminded that the subject-matter of chemistry is 'the differences and relations of matter,'[1] and not the properties of this or that isolated system of matter.

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[1] Phrase used by Clerk Maxwell in a letter to Mr L. Campbell. See his *Life* (Condensed Ed.), p. 110.

SECTION II. *Affinity.*

220. We have seen that one form which the 'law of maximum work' has assumed is expressed in the statement that a chemical change always proceeds in a direction such that the strongest affinities of the reacting bodies are satisfied.

If the criticisms brought against the 'law' are admitted this form of it cannot be accepted.

But, we inquire: is it possible to obtain relative measurements of *affinities* by determining the thermal values of chemical operations? We learned in Chap. III. (pars. 102—110) the use which Thomsen has made of such determinations for finding the quantitative distribution of a base between two acids, and the conclusions which that naturalist has thence drawn regarding the relative affinities of acids. But can any more light be thrown on the subject of affinities by thermal methods of inquiry? Do chemical changes occur in such a way that the strongest affinities between the atoms of the reacting bodies are satisfied?

Now the word atom is here used with a wider and vaguer meaning than ought strictly speaking to be assigned to it. Unless we are prepared to apply the terminology of the molecular theory to solids and liquids we need scarcely trouble ourselves with such a question as that we have asked. The phrase 'satisfaction of atomic affinities' is also vague. But let us employ the expression and see if in trying to answer the question any more definite meaning can be given to the terms in which it is put[1].

221. Do chemical changes occur in such a way that the strongest affinities between the atoms of the reacting bodies are satisfied?

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[1] In papers on thermal chemistry the term affinity is sometimes used in a very misleading manner. If one element *A* combines with another *B* with evolution of so much heat, and a third element *C* combines with *B* with evolution of so much more heat, it is said that the affinity of *C* for *B* is greater than that of *A* for *B*, and greater by the difference between the two quantities of heat. This use of the term affinity seems to me to be utterly erroneous. But affinity is one of these chameleon-like words which do so much harm in science.

If we answer this question in the affirmative we should also probably say that the phrase 'satisfaction of the strongest affinities between the atoms' is synonymous with 'production of that configuration of atoms (starting from a specified configuration) which is attended with the maximum evolution of heat, or, at any rate, with the maximum running down of energy.'

222. Let atomic affinity mean the potential energy of atoms. Let two monovalent atoms, *A* and *B*, mutually attract each other with the production of a molecule *AB*; there is a change of potential energy (i.e. affinity) into kinetic energy which leaves the system in the form of heat. Now let a third monovalent atom, *C*, approach the molecule *AB*, and let the affinity of *A* for *C* be greater than that of *A* for *B*. When *AB* and *C* are a certain distance apart the attraction of *A* for *C* will exceed that of *A* for *B*, the molecule *AC* will be formed and the atom *B* will remain uncombined. The formation of *AC* will be attended by a change of potential into kinetic energy which will again appear as heat. But unless this second quantity of heat is greater than that evolved in the formation of the original molecule *AB* from the atoms *A* and *B*, the decomposition of *AB* could not occur. Hence atoms with stronger affinities replace those with weaker affinities, and the relative strengths of these affinities are measured by the quantities of heat evolved in the combinations of the atoms, provided affinity is synonymous with potential energy of atoms considered as at rest[1].

223. But if the theory of molecules and atoms teaches anything, it teaches that the atoms are not at rest; but that they, no less than the molecules themselves, are in motion. Of the states of molecular motion we know little or nothing; of the atomic motions we know even less. Probably the motions of the individual molecules which compose a gaseous mass, both the translatory motions of the molecules as wholes and also the rotatory motions of their parts, differ considerably from the mean motion of the whole mass of molecules. A feasible hypothesis is, that there is a constant change of potential atomic energy

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[1] For the statement of this argument and of that which follows I am indebted to L. Meyer's *Die modernen Theorien der Chemie*, 442—447 (4th Ed.).

into kinetic atomic energy, and *vice versa*, due to the vibratory motions of the atoms which constitute the molecules. If this is so, any specified molecule must be more ready to undergo change at certain times than at other times. Hence a given compound may be decomposed by the action of another compound under certain specified conditions and not under other specified conditions. Proceeding on the lines of this hypothesis let us consider, as before, the diatomic molecule AB acted on by the atom C. The result of the collision of AB and C will vary in accordance with the distribution of the kinetic and potential energies in AB at the moment of collision. Let us suppose that A and B are at their furthest distance apart, i.e. the potential energy of A and B is at a maximum and the kinetic energy at a minimum. Let C now come into contact with AB and carry off A in combination with itself; a part of the kinetic energy of C will be employed in overcoming the affinity of A for B, and this action will be accompanied by evolution of heat (or other form of kinetic energy). But the rest of the kinetic energy of C remains in the new molecule AC. Whether the decomposition of AB by C shall or shall not occur does not then depend on whether $[A, B] > [A, C]$, or $[A, C] > [A, B]$, but on the relative affinities of A and C for B: what C wants in potential energy (i.e. affinity) it supplies in the form of kinetic energy. If we pass from the consideration of isolated atoms to that of masses of two reacting bodies we find that the decomposition of one by the other must depend on many conditions among which affinity,—i.e. in the present view mutual atomic attraction—is only one. If the conception of constant change of potential into kinetic energy and *vice versa* of the atoms in the molecule is accepted, then the mutual attraction between A and B may be such that these two atoms hold together for long, because the conditions under which C can decompose AB are seldom attained. The temperature, the relative masses of the two bodies, the presence of a third body, &c., will largely condition the action of C on AB[1].

224. The difficulties of this investigation are very great. Does the heat evolved in a chemical reaction represent change

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[1] For more details see L. Meyer, *loc. cit.* 446.

of potential energy of the atoms into the thermal form of kinetic energy? Or is the heat more probably due to the change of a higher form of kinetic energy of the atoms into heat? Or does the quantity of heat evolved afford no measure, or at any rate no generally applicable trustworthy measure, of the change of higher into lower forms of atomic energy which accompanies a chemical operation? We cannot answer these questions. We can scarcely as yet suggest the outlines of answers.

225. A definite meaning for the term affinity has been introduced into chemical science by the researches of Guldberg and Waage. This meaning is independent of any hypothesis regarding the relations of the kinetic and potential energies of the atoms in the chemical molecule; indeed it is independent of any theory of the structure of matter.

In the *Essai de Statique Chimique* published in 1803 Berthollet said "Toute substance qui tend à entrer en combinaison agit en raison de son affinité et de sa quantité" (*loc. cit.* 1. 2). This statement has been extended and rendered more exact by the researches of the Norwegian naturalists Guldberg and Waage[1].

In a simple decomposition of the form $AB + C = AC + B$, the formation of AC is chiefly brought about by the attraction between A and C; but there are also attractions between the other substances A and B, AC and B, &c. Looking at these attractions from the point of view of one of the attracting bodies we may say that A exerts force on C, AC exerts force on B, B exerts force on A, and so on. The force by the action of which AC is finally produced is the resultant of these various forces. This resultant force may be regarded as constant for a definite temperature. It is called by Guldberg and Waage the *coefficient of affinity* for the reaction $AB + C = AC + B$. In the same way in the double decomposition $AB + CD = AC + BD$ the force which brings about the formation of AC and BD is the resultant of the various forces at work, e.g. the force exerted by A on B, by A on C, by A on D, by C on D, &c.; this resultant force is called the *coefficient of affinity* for the reaction formulated above.

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[1] *Études sur les Affinités Chimiques* (Christiania, 1867); and (in continuation) *J. für prakt. Chemie* (2) **19**. 69.

But this coefficient of affinity may be resolved into two parts. Let two bodies A and B react, in equivalent quantities, under such conditions that the system is free to settle down into equilibrium (e.g. in dilute aqueous solution), two new bodies, A' and B', will be produced; but when equilibrium is established the system will consist of certain quantities of the four bodies A, B, A', and B'. The force (itself the resultant of various forces) which brings about the formation of A' and B' from A and B is held in equilibrium by the force (likewise the resultant of various forces) which brings about the re-formation of A and B from A' and B'. The first of these forces is called the *coefficient of affinity* for the direct reaction $A + B = A' + B'$; the second is called the *coefficient of affinity* for the reverse reaction $A' + B' = A + B$.

Let us designate the coefficient of affinity of the direct change by κ, and that of the reverse change by κ'. All the measurements which have been made of such a change as we are now dealing with, viz.

$A + B \rightleftarrows$[1] $A' + B'$

have shewn that the equilibrium of the system at a specified temperature is to a great extent conditioned by the relative masses of A and B. Guldberg and Waage use the expression *active mass* of A or B, &c. to mean the number of equivalents of A or B, &c. in a unit of volume of the reacting system, e.g. in 1000 c.c. of the aqueous solution of A or B, &c. employed. Guldberg and Waage state that the total resultant force for either the direct or reverse change, when equilibrium is established, is proportional to the product of the constant κ, that is the coefficient of affinity for the change (be it direct or reverse) and the active masses, A, B, A', or B' as the case may be. Let the system have settled down into equilibrium; let the active mass of A now present be p, the active mass of B be q, the active mass of A' be p', and the active mass of B' be q'. Then when equilibrium is established

$$\kappa \,.\, p \,.\, q = \kappa' . p' . q'.$$

Now it is possible to determine experimentally the values of

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[1] This notation for reversible or partially reversible changes is suggested by *van 't Hoff* (*Études de Dynamique Chimique* [1884], p. 8).

p, q, p', and q' for a given system[1]; when this is done the ratio $\kappa : \kappa'$ can be calculated. Suppose this has been done; it is then possible to calculate the values of p, q, p', and q' for any initial quantities of the four reacting bodies; in other words it is possible to calculate the number of equivalents of A, B, A', and B' present in the system when equilibrium is established, provided the number of equivalents of each of these bodies originally present is known. For, let P, Q, P', and Q' represent the number of equivalents of A, B, A', and B' present before the action begins, and let x equal the number of equivalents of A and B trans~~ferred~~formed into A' and B' when equilibrium is established, and assuming the total volume of the system to be constant throughout the process and to be equal to V, then

$$p = \frac{P-x}{V}, \quad q = \frac{Q-x}{V}, \quad p' = \frac{P'+x}{V}, \quad q' = \frac{Q'+x}{V}.$$

Then substituting these values for p, q, p', and q' in the equation of equilibrium, and multiplying by V^2 we get

$$\kappa (P-x)(Q-x) = \kappa' (P'+x)(Q'+x).$$

But the ratio $\kappa : \kappa'$ has been already determined, and P, Q, P', and Q' are known by direct observation; hence x can be found by calculation, and the calculated values of x, for different values of P, Q, &c. can be compared with the observed values, and in this way the applicability of the general equation of equilibrium can be tested. When the value of the ratio $\kappa : \kappa'$ has been thus determined for one system, a new system may be employed in which κ again occurs along with another coefficient of affinity κ''; the ratio $\kappa : \kappa''$ may thus be found. This process may be repeated for a number of systems and thus values may be found for various coefficients of affinity in terms of some one coefficient of affinity taken as unity.

226. Ostwald has made an extensive series of determinations of the coefficients of affinity of reactions between pairs of acids and a specified base[2]. One very important result of these researches is that the coefficient of affinity of such a reaction as

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[1] For methods by which this may be done see Guldberg and Waage *loc. cit.* also Ostwald, *J. für prakt. Chemie*, (2), **25.** 1.

[2] Ostwald's papers are to be found in *J. für prakt. Chemie*, (2) **16.** 385 : **18.** 328 : **19.** 468 : **22.** 251 : **23.** 209 and 517 : **24.** 486 : **27.** 1 : **28.** 449 : **29.** 385.

$AB + C = AC + B$,—where AB is a compound of an acid B with the base A, and C is another acid,—consists of two parts, one dependent on the nature of the acids, and the other on the nature of the base. By keeping the base constant and varying the acids Ostwald has made a series of determinations of what he calls the *relative affinities* of acids. Further research has shewn that these relative affinities of acids are constants of the utmost importance, inasmuch as they appear to quantitatively condition every chemical change in which the acids take part. Ostwald's investigations have, I think, established the assertion,—or at any rate established a very large probability in favour of the assertion,—that the specific intensity of any action brought about by an acid is conditioned by the value of the relative affinity of that acid.

But even if this assertion is not at present accepted there can be no doubt, in the face of the experiments of Guldberg and Waage, Ostwald, Thomsen, and others, that determinations of the relative affinities of acids are of the utmost value.

When we consider the wide-spreading results which are likely to follow the cultivation of this field of inquiry we cannot but be impressed with the importance of prosecuting further researches on the lines of those already so successfully conducted by the naturalists whom I have named.

227. One main difficulty is to find suitable methods for prosecuting these inquiries[1]. Now thermal chemistry presents us with methods for determining the relative affinities of acids. We have seen (Chap. III. pars. 103—107) how Thomsen found values for what he calls the relative *avidities* of various acids. But the avidity of an acid is the same constant as the affinity. The amount of an action between two acids and a base is conditioned by (1) the relative affinities (or avidities), and (2) the active masses of the acids.

We have glanced at the thermal method whereby the relative affinity of an acid may be determined; let us now look at this method in the light of the theory of affinity of Guldberg and Waage[1].

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[1] Chemical changes must be chosen which are free from secondary reactions; special experimental methods must be devised, and many difficulties must be surmounted. For a general account of what has been done by Ostwald and others see the author's *Principles of Chemistry*, Book II., Chap. III.

228. For the convenience of subsequent treatment, Thomsen writes the equation

$$\kappa(P-x)(Q-x)=\kappa'(P'+x)(Q'+x)$$

as

$$\kappa(\alpha-x)(\beta-x)=\frac{1}{\kappa_1}(\gamma+x)(\delta+x).$$

Then putting the product $\kappa \,.\, \kappa_1 = n^2$ he deduces the following equation for finding the value of x,

$$x=\frac{n^2(\alpha+\beta)+\gamma+\delta-\sqrt{[n^2(\alpha+\beta)+\gamma+\delta]^2-4(n^2-1)(n^2\alpha\beta-\gamma\delta)}}{2(n^2-1)}.$$

The value of n must now be found. This may be done by using the experimental results obtained in the action of one equivalent of sodium sulphate on one equivalent of nitric acid. In this case

$$\alpha=\beta=1;\quad \gamma=\delta=0;$$

and the above formula gives the value

$$x=\frac{n}{n+1}.$$

But Thomsen's results already referred to (Chap. III. par. 107) shewed that in the action of equivalent quantities of nitric and sulphuric acids on soda in dilute aqueous solution $x=\frac{2}{3}$; that is to say, two-thirds of the soda combine with the nitric acid and one-third with the sulphuric acid. Hence

$$x=\frac{n}{n+1}=\tfrac{2}{3};\text{ and therefore } n=2.$$

This quantity n is the ratio of the avidities of the two acids acting simultaneously on the same base.

Substituting the value of n thus found in the foregoing equation for finding x, we have

$$x=\tfrac{1}{6}\{4(\alpha+\beta)+\gamma+\delta-\sqrt{[4(\alpha+\beta)+\gamma+\delta]^2-12(4\alpha\beta-\gamma\delta)}\}.$$

This formula may be used for finding the value of x, that is the amount of chemical change, in all reactions between sulphuric and nitric acids and soda in dilute aqueous solutions.

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[1] See Thomsen *loc. cit.* I. 118—125.

Let R = the thermal value of a specified reaction. Let $AB = Na_2SO_4Aq$; $A'B = Na_2N_2O_6Aq$; $A = H_2SO_4Aq$; and $A' = H_2N_2O_6$[1]Aq. Then let these compounds react in different proportions:—

$$R = [\alpha AB,\ \beta A',\ \gamma A,\ \delta A'B].$$

When the system has settled down into equilibrium the distribution of the salts is represented as

$$(\alpha - x)AB + (\beta - x)A' + (\gamma + x)A + (\delta + x)A'B.$$

The formula given above for finding x, when the values of α, β, γ, and δ vary, may now be applied.

Thomsen's experiments furnish four groups of results.

229. I. $R = [AB, \beta A']$; or R = the thermal value of the action of one equivalent of sodium sulphate and β equivalents of nitric acid.

Here $\alpha = 1$; $\gamma = \delta = 0$; and

$$x = \tfrac{2}{3}(1 + \beta - \sqrt{(1+\beta)^2 - 3\beta}).$$

Neglecting those parts of the chemical change the thermal values of which have been shewn experimentally to be almost equal to zero, we have

$$[AB, \beta A'] = x([A', B] - [A, B]) + (1 - x)[AB, \tfrac{x}{1-x}A].$$

Substituting the observed values, viz.

$$[A', B] = 27{,}234 \text{ and } [A, B] = 31{,}378$$

we have

$$[AB, \beta A'] = -4144\,x + (1 - x)\left[AB, \frac{x}{1-x}A\right].$$

The following table shews the observed and calculated thermal values of this change for varying values of β.

β	x	$(1-x)\left[AB, \frac{x}{1-x}A\right]$	$[AB, \beta A']$	
			observed	*calculated*
$\frac{1}{8}$	0·121	−424	− 904	− 924
$\frac{1}{4}$	0·232	−694	−1616	−1656
$\frac{1}{2}$	0·423	−910	−2584	−2662
1	0·667	−784	−3504	−3546
2	0·845	−446	−4052	−3948
3	0·903	−296	−4100	−4038

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[1] *This is the same notation as was used before (Chap.* III. *par. 106).*

The greatest difference between the observed and calculated numbers amounts to 104 units, or only 3 per thousand of the value of the heat of neutralisation of either acid.

230. II. $R = [AB\gamma A, 2A']$ or $= [AB, \gamma A, 2A'] - [AB, \gamma A']$.

That is, $R =$ the thermal value of the action of one equivalent of sodium sulphate mixed with γ equivalents of sulphuric acid on two equivalents of nitric acid. Here $\alpha = 1$; $\beta = 2$; $\delta = 0$; and

$$x = \frac{12 + \gamma - \sqrt{(12 + \gamma)^2 - 96}}{6}.$$

Substituting the observed values we have

$$[AB\gamma A, 2A'] = -4144\, x + (1 - x) \left[AB, \frac{\gamma + x}{1 - x} A\right] - [AB, \gamma A].$$

The observed and calculated values of the change, when γ varies from 0 to 3, are presented in the following table.

γ	x	$(1-x)\left[AB, \frac{\gamma+x}{1-x} A\right]$	$[AB\gamma A, 2A']$	
			observed	*calculated*
0	0·845	− 446	−4052	−3948
1	0·742	− 762	−1956	−1964
2	0·667	− 998	−1328	−1424
3	0·607	−1194	−1040	−1102

The greatest difference between the observed and calculated numbers is again 104 units, or only 3 per thousand of the value of the heat of neutralisation of either acid.

231. The third and fourth groups of results give data for finding

III. $R = [\frac{1}{2}AB, \frac{1}{2}A'B, \beta A']$;

IV. $R = [A'B, \gamma A]$.

The observed results agree, to within 2 per thousand of the heat of neutralisation, with those calculated by the aid of the formula which Thomsen has deduced from the fundamental equation of Guldberg and Waage's theory. Thomsen has also applied this method to the reactions occurring between hydrochloric acid, soda, and sulphuric acid; the calculated and observed numbers agree very closely.

232. This investigation made by Thomsen on the one hand affords an independent verification of the theory of Guldberg and Waage, and on the other hand shews that thermal methods may with advantage be used in investigating the problems of affinity, provided the word affinity is employed with at least some such meaning as is given to it by the Norwegian naturalists. It seems to me very doubtful whether measurements of the quantities of heat absorbed or evolved in chemical operations can, in the present state of knowledge, help much towards gaining clearer notions of affinity regarded as an action and reaction between atoms.

233. We have repeatedly had occasion to notice the appearance of a constant number in considering differences between the thermal values of comparable reactions. If the term affinity is employed to mean the resultant of the actions of the forces which come into play in a definite and simple chemical change, after eliminating as far as possible all physical and secondary changes, then it is possible that the differences between the thermal values of such definite and simple chemical processes may represent differences between the affinities concerned in these processes. As an instance of such differences we may take the following numbers:—

[H, X] gaseous.
$X = \mathrm{Cl} =$ 22,000 units.
$X = \mathrm{Br} =$ 12,000 „
$X = \mathrm{I} = -$ 1,530 „

The probable conclusion is, that the differences between the affinities concerned in the three comparable reactions, viz. formation of gaseous hydrochloric, hydrobromic, and hydriodic acids from their gaseous elementary constituents, are expressed by the differences between the numbers 22, 12, and $-1{\cdot}5$. If this conclusion has any warranty then the differences between the thermal values of analogous simple chemical changes in which the same elements take part should be capable of being represented as multiples of a common number. That this is so, we have had occasion to notice more than once[1]. Here are some of the data:—

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[1] See e.g. Chap. III. par. 112.

(1) $[\mathrm{H}, X, \mathrm{Aq}]$. $X = \mathrm{Cl} = 39{,}315$; $X = \mathrm{Br} = 28{,}370$; $X = \mathrm{I} = 13{,}170$;

$$\therefore [\mathrm{H}, \mathrm{Cl}, \mathrm{Aq}] - [\mathrm{H}, \mathrm{Br}, \mathrm{Aq}] = 10{,}945$$

and
$$[\mathrm{H}, \mathrm{Cl}, \mathrm{Aq}] - [\mathrm{H}, \mathrm{I}, \mathrm{Aq}] = 26{,}145.$$

(2) $[\mathrm{K}, X, \mathrm{Aq}]$. $X = \mathrm{Cl} = 101{,}170$; $X = \mathrm{Br} = 90{,}230$; $X = \mathrm{I} = 75{,}020$;

$$\therefore [\mathrm{K}, \mathrm{Cl}, \mathrm{Aq}] - [\mathrm{K}, \mathrm{Br}, \mathrm{Aq}] = 10{,}940$$

and
$$[\mathrm{K}, \mathrm{Cl}, \mathrm{Aq}] - [\mathrm{K}, \mathrm{I}, \mathrm{Aq}] = 26{,}150.$$

Also
$$[\mathrm{Na}, \mathrm{Cl}, \mathrm{Aq}] - [\mathrm{Na}, \mathrm{Br}, \mathrm{Aq}] = 10{,}930$$

and
$$[\mathrm{Na}, \mathrm{Cl}, \mathrm{Aq}] - [\mathrm{Na}, \mathrm{I}, \mathrm{Aq}] = 26{,}150.$$

The difference between the heat of formation, in solution, of a chloride and a bromide of the same element is 10,940 units; and the difference between the heat of formation, in solution, of a chloride and an iodide of the same element is 26,150 units. These differences reappear in the following data:—

$$\left.\begin{aligned}[\mathrm{M}, \mathrm{Cl}^2, \mathrm{Aq}] - [\mathrm{M}, \mathrm{Br}^2, \mathrm{Aq}] = 2 \times 10{,}940\\ [\mathrm{M}, \mathrm{Cl}^2, \mathrm{Aq}] - [\mathrm{M}, \mathrm{I}^2, \mathrm{Aq}] = 2 \times 26{,}150\end{aligned}\right\} \text{ when } \mathrm{M} = \mathrm{Ca}, \mathrm{Sr}, \text{ or } \mathrm{Cu}.$$

Let us now keep the halogen constant but vary the positive radicle, always however replacing one radicle by another chemically comparable with it. Thus:—

$$[\mathrm{K}, X, \mathrm{Aq}] - [\mathrm{Na}, X, \mathrm{Aq}] = \begin{cases} 4{,}660 \text{ when } X = \mathrm{Cl}, \\ 4{,}650 \text{ when } X = \mathrm{Br}, \\ 4{,}620 \text{ when } X = \mathrm{I}. \end{cases}$$

And $[\mathrm{Sr}, X^2, \mathrm{Aq}] - [\mathrm{Ca}, X^2, \mathrm{Aq}] = 2 \times 4{,}020$ when $X = \mathrm{Cl}$, Br, or I.

Another constant difference is exhibited in these numbers:—

$$[X\mathrm{SO}^4\mathrm{Aq}, \mathrm{Mg}] \begin{cases} X = \mathrm{Fe} = 5 \times 17{,}410 \\ X = \mathrm{Cu} = 7 \times 17{,}810 \\ X = \mathrm{Zn} = 4 \times 18{,}120 \\ X = \mathrm{Cd} = 5 \times 18{,}280. \end{cases}$$

$$[X\mathrm{Cl}^2\mathrm{Aq}, \mathrm{Mg}] \begin{cases} X = \mathrm{Fe} = 5 \times 17{,}390 \\ X = \mathrm{Cu} = 7 \times 17{,}750 \\ X = \mathrm{Zn} \times 4 \times 18{,}520 \\ X = \mathrm{Cd} = 5 \times 18{,}130. \end{cases}$$

Here we might venture to say that the affinities concerned in the replacement of iron, copper, zinc, and cadmium, by magnesium, from aqueous solution of the sulphates or chlorides of these four metals, are approximately in the ratio 5 : 7 : 4 : 5.

The problems of affinity have scarcely as yet been clearly and definitely stated. When this is done they will already be partly solved.

Concluding Remarks.

We have been trying to gain some knowledge of the mutual relations of chemical and thermal phenomena. Each chemical change has presented us with a two-sided phenomenon, a change of matter and a change of energy; we have made some attempts to correlate these two transformations. We have found it necessary accurately to define the initial and final states of every chemical system, the energy-changes of which have been considered. As chemical occurrences present changes of material configuration they appear to involve transformations of potential as well as of kinetic energy; hence arises a great difficulty in the study of the energetics of these occurrences.

In attempting to apply dynamical principles to thermochemical phenomena we have continually met with difficulties. How are we to measure the force exerted by one chemical system on another, or by one part of a system on another part of the same system? In what direction are the forces applied whose actions we wish to study? What shall be our unit of force?

We have considered various classes of chemical occurrences with the view of connecting changes of composition with changes of properties especially as the latter are measured by changes of energy; with the view that is to say of attempting to solve the fundamental question of chemistry.

A thermal study of isomeric changes is likely to yield important results in this direction.

For the most part we have found it necessary to interpret thermochemical data apart from any definite theory of the structure of matter; but at the same time we have tried to proceed on the broad lines of the molecular theory.

The phenomena of dissociation presented a class of occurrences at once chemical and physical. These phenomena, more I suppose than any others in thermal chemistry, are capable of treatment by thermodynamical methods. At the same time they present interesting aspects to the student of pure chemistry.

Then we were led to consider the great problems of affinity. In chemistry we must not be content with knowing the composition of this compound or that, or of this system or that, we must not be content even with knowing the changes which occur in these systems under defined conditions. We must ask: What are the forces at work in these changes? What are the laws of these forces? Can we generalise the observed facts regarding the mutual actions of chemical systems? In a word, what can we know of chemical affinity? I have tried to shew that thermal methods help us here, but that one must be careful to state the problems in such terms as render possible the application of the data of thermal chemistry.

We examined the widest generalisation which has as yet been made connecting losses of energy with changes of chemical composition; and we found it too wide.

Of more promise than the law of maximum work, Thomsen's researches on the relative affinities of acids open up a large and most important field of inquiry. Again and again we have had occasion to turn to this eminent student of nature for data and for the interpretation of data. In his *Thermochemische Untersuchungen* Thomsen has raised an enduring monument to himself and has done much to rescue chemistry from sinking to the rank of mere narrative.

Chemists have again entered on the path of research opened up for them by Berthollet in the early years of this century. They are making quantitative measurements of affinities, and so are gaining series of numbers each of which expresses many facts and suggests many more. When we have accumulated measurements of affinities and can compare these values with the atomic and molecular weights of the elements and compounds whose affinities are known, we shall have made a real advance towards understanding the connections which undoubtedly exist between chemical composition on the one hand and power of doing, or function, on the other.

But thermal chemistry is yet in its beginning. The facts suggest more questions than they answer. Facts here go hand in hand with theory. We are not bound hand and foot by the structural formulae which exert so deadly a tyranny in many departments of chemistry. Thermal chemistry wants more investigation and more interpretation of the facts it has already amassed. For the bare facts are insufficient: as soon as we look at natural facts we begin to classify; so we connect and separate; and then we theorise.

APPENDICES.

APPENDIX I.

DATA RELATING TO HEATS OF FORMATION AND HEATS OF COMBUSTION.

I. *Heats of formation of compounds of non-metals (including arsenic, antimony, and bismuth) according to the investigations of Thomsen*[1].

Unless the contrary is expressed, the thermal values contained in the following tables are valid for a temperature of 18—20°C at constant pressure, and for the normal state of aggregation of constituents and products at that temperature.

HYDROGEN.

Reaction	Thermal value	Remarks
$[Cl, H]$	22,000	
$[Br, H]$	8,440	These thermal values are valid for the normal state of the elements and products. The heat of fusion and heat of vaporisation for one formula-weight of H_2O are, according to Regnault, 1,440 and 9,660 units (at 100°) respectively.
$[I, H]$	− 6,040	
$[O, H^2]$	+ 68,360	
$[S, H^2]$	4,740	
$[N, H^3]$	11,890	
$[C, H^4]$	21,750	
$[C^2, H^6]$	28,560	
$[C^2, H^4]$	− 2,710	
$[C^2, H^2]$	− 48,170	
$[C^6, H^6]$	+ 6,090 − 1,110	Product is gaseous benzene.

$[Cl, H]$	$21,984 + 0{\cdot}9 \times t$	Valid for the temperature t if both the elements and the products are assumed to be gaseous.
$[Br, H]$	$12,244 + 0{\cdot}9 \times t$	
$[I, H]$	$- 605 + 0{\cdot}9 \times t$	
$[O, H^2]$	$57,903 + 1{\cdot}6 \times t$	
$[S, H^2]$	$8,942 + 1{\cdot}9 \times t$	
$[N, H^3]$	$11,792 + 5{\cdot}0 \times t$	

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[1] *Thermochemische Untersuchungen*, **2.** 397—412.

Hydrogen peroxide, H_2O_2.

$[H^2, O^2, Aq]$	45,300	Formation and decomposition of hydrogen peroxide in aqueous solution.
$[H^2O, O, Aq]$	− 23,060	
$[H^2O^2\ Aq, H^2]$	+ 91,420	

OXYGEN.

Reaction	Thermal value	Remarks
$[H^2, O]$	68,360	Product, liquid.
$[Cl^2, O]$	− 17,930	„ gaseous.
$[N^2, O]$	− 17,470	» »
$[N, O]$	− 21,575	» »
$[C, O]$	+ 29,000	» »
$[S, O^2]$	71,080	» »
$[Se, O^2]$	57,080	„ crystalline.
$[N, O^2]$	− 2,005	„ gaseous.
$[C, O^2]$	+ 96,960	For amorphous carbon, according to Favre and Silbermann.
$[S, O^3]$	103,240	Product, liquid.
$[As^2, O^3]$	154,670	„ solid.
$[I^2, O^5]$	45,030	» »
$[P^2, O^5]$	369,900	» »
$[As^2, O^5]$	219,380	» »

CHLORINE.

1. *Various chlorides.*

Reaction	Thermal value	Remarks
$[H, Cl]$	22,000	Of the compounds of chlorine whose heats of formation are given here, HCl and Cl_2O are gaseous at a temperature of 18—20°, while at the same temperature ICl_3, $SeCl_4$, $TeCl_4$, PCl_5, $SbCl_3$, and $BiCl_3$ are solid, and all the rest liquid. The thermal value is valid for the state of aggregation normal to the bodies at the temperature mentioned, and for rhombic sulphur, amorphous selenion, metallic tellurium, ordinary phosphorus, and amorphous carbon.
$[I, Cl]$	5,830	
$[I, Cl^3]$	21,490	
$[O, Cl^2]$	− 17,930	
$[S^2, Cl^2]$	+ 14,260	
$[Se^2, Cl^2]$	22,150	
$[Se, Cl^4]$	46,160	
$[Te, Cl^4]$	77,380	
$[P, Cl^3]$	75,300	
$[P, Cl^5]$	104,990	
$[As, Cl^3]$	71,380	
$[Sb, Cl^3]$	91,390	
$[Sb, Cl^5]$	104,870	
$[Bi, Cl^3]$	90,630	
$[C, Cl^4]$	28,230	Product, liquid.
	21,030	„ gaseous.
$[C^2, Cl^4]$	6,000	„ liquid.
	− 1,150	„ gaseous.

2. *Hydrochloric acid*, HCl.

[H, Cl]	22,000	Product, gaseous.
[H, Cl, Aq]	39,315	„ aqueous solution.
[HCl, Aq]	17,315	Heat of solution.

3. *Hypochlorous acid*, HClO.

[Cl^2, O]	– 17,930	Gaseous compound.
[Cl^2, O, Aq]	– 8,490	Aqueous solution.
[Cl^2O, Aq]	+ 9,440	Heat of solution.
[Cl, O, H, Aq]	29,930	ClOH formed in aqueous solution.
[NaOHAq, ClOHAq]	9,980	Heat of neutralisation.

4. *Chloric acid*, $HClO_3$.

[Cl^2, O^5, Aq]	– 20,480	Cl_2O_5 formed in aqueous solution.
[Cl, O^3, H, Aq]	+ 23,940	ClO_3HAq formed from its elements.
[ClOHAq, O^2]	– 5,990	ClO_3HAq formed from ClOHAq.
[HClAq, O^3]	– 15,380	ClO_3HAq formed from HClAq.

5. *Potassium chlorate*, $KClO_3$.

[K, Cl, O^3]	95,860	Cryst. $KClO_3$ formed from its elements.
[KCl, O^3]	– 9,750	Cryst. $KClO_3$ formed from KCl and O_3.
[$KClO^3$, Aq]	– 10,040	Heat of solution.
[K, Cl, O^3, Aq]	+ 85,820	$KClO_3Aq$ formed from its elements.
[KClOAq, O^2]	– 2,210	„ „ from KClOAq and O_2.
[KClAq, O^3]	– 15,370	$KClO_3Aq$ „ from KClAq and O_3.
[KOHAq, $HClO^3Aq$]	+ 13,760	Heat of neutralisation.

6. *Constants of Oxidation.*

2[H, Cl, Aq] – [H^2, O]	10,270	Oxidation by water and chlorine gas.
[H, Cl, Aq] – [H, Cl, O, Aq]	9,380	Oxidation by decomposition of HClOAq to form HClAq.
[H, Cl, Aq] – [H, Cl, O^3, Aq]	15,380	Oxidation by decomposition of $HClO_3Aq$ to form HClAq.
[Cl^2, Aq]	2,600	Heat of solution of chlorine.

BROMINE.

Reaction	Thermal value	Remarks	
1. *Hydrobromic acid*, HBr.			
[H, Br]	8,440	Formation of the gaseous compound	from liquid bromine.
[H, Br, Aq]	28,380	Formation of the aqueous solution	
[HBr, Aq]	19,940	Heat of solution.	
2. *Hypobromous acid*, HBrO.			
[Br^2, O, Aq]	−16,190	Formation of Br_2O and BrOH in aqueous solution, from the elements.	
[Br, O, H, Aq]	+26,080		
3. *Bromic acid*, $HBrO_3$.			
[Br^2, O^5, Aq]	−43,520	Formation of Br_2O_5 and BrO_3H in aqueous solution, from the elements.	
[Br, O^3, H, Aq]	+12,420		
[HBrAq, O^3]	−15,960	Formation of $HBrO_3Aq$ by oxidation of HBrAq.	
4. *Potassium bromate*, $KBrO_3$.			
[K, Br, O^3]	84,060	Formation of cryst. $KBrO_3$ from its elements.	
[KBr, O^3]	−11,250	Formation of cryst. $KBrO_3$ from KBr and O_3.	
[$KBrO^3$, Aq]	− 9,760	Heat of solution.	
[K, Br, O^3, Aq]	+74,300	Formation of $KBrO_3Aq$ from its elements.	
[KBrAq, O^3]	−15,930	Formation of $KBrO_3Aq$ from KBrAq and O_3.	
[KOHAq, $HBrO^3Aq$]	13,780	Heat of neutralisation.	
5. *Constants of Oxidation.*			
2[H, Br, Aq]−[H^2, O]	−11,600	Oxidation by bromine and water.	
2[H, BrAq]−[H^2, O]	−12,680	„ by bromine water.	
[Br^2, Aq]	+ 1,080	Heat of solution of bromine.	

IODINE.

Reaction	Thermal value	Remarks
1. *Hydriodic acid*, HI.		
$[H, I]$	− 6,040	Formation of gaseous HI.
$[H, I, Aq]$	+ 13,170	„ „ HI in aqueous solution.
$[HI, Aq]$	19,210	Heat of solution.
2. *Iodic acid*, HIO_3.		
$[I^2, O^5]$	45,030	Formation of I_2O_5 and IO_3H from the elements.
$[I, O^3, H]$	57,960	
$[I^2, O^5, H^2O]$	47,570	
$[I^2, O^5, Aq]$	43,240	Formation of the same bodies in aqueous solution.
$[I, O^3, H, Aq]$	55,800	
$[I^2O^5, H^2O]$	2,540	Formation of the hydrate.
$[I^2O^5, Aq]$	− 1,790	Heats of solution of the anhydride and the acid.
$[IO^3H, Aq]$	− 2,170	
$[HIAq, O^3]$	42,630	Formation of IO_3HAq and IO_3H by oxidation of HIAq and HI.
$[HI, O^3]$	64,000	
3. *Potassium iodate*, KIO_3.		
$[K, I, O^3]$	124,490	Formation of cryst. KIO_3 from its elements.
$[KI, O^3]$	44,360	Formation of cryst. KIO_3 from KI and O_3.
$[KIO^3, Aq]$	− 6,780	Heat of solution.
$[K, I, O^3, Aq]$	117,710	Formation of KIO_3Aq from its elements.
$[KIAq, O^3]$	42,690	Formation of KIO_3Aq from KIAq and O_3.
$[KOHAq, HIO^3Aq]$	13,810	Heat of neutralisation.
4. *Periodic acid*, H_5IO_6.		
$[I, O^6, H^5]$	185,780	Formation of crystallised H_5IO_6 from its elements.
$[I, O^6, H^5, Aq]$	184,400	Formation of periodic acid in aqueous solution, from the constituents indicated.
$[I, O^4, H, Aq]$	47,680	
$[I^2, O^7, Aq]$	27,000	
$[IO^6H^5, Aq]$	− 1,380	Heat of solution.
$[IHAq, O^4]$	34,510	Formation by oxidation of solution of hydriodic acid.
$[KOHAq, H^5IO^6Aq]$	5,150	Heats of neutralisation.
$[2KOHAq, H^5IO^6Aq]$	26,590	

5. *Iodine chlorides*, ICl and ICl_3.

$[I, Cl]$	5,830	Formation of liquid ICl.
$[I, Cl^3]$	21,490	„ „ solid ICl_3.
$[ICl, Cl^2]$	15,660	„ „ ICl_3 from ICl and Cl_2.

SULPHUR (rhombic).

Reaction	Thermal value	Remarks
1. *Sulphuretted hydrogen*, H_2S.		
$[H^2, S]$	4,740	Formation of gaseous H_2S.
$[H^2, S, Aq]$	9,300	„ „ H_2S in aqueous solution.
$[H^2S, Aq]$	4,560	Heat of solution.
2. *Sulphurous anhydride*, SO_2.		
$[S, O^2]$	71,080	Gaseous product (for monoclinic sulphur = 71,720).
$[S, O^2]$	77,280	Liquid product (latent heat 6,200).
$[S, O^2, Aq]$	78,780	Formation in aqueous solution.
$[SO^2, Aq]$	7,700	Heat of solution.
$[SO^2, Aq]$	1,500	Heat of solution of liquid SO_2.
$[2NaOHAq, SO^2Aq]$	28,970	Heat of neutralisation.
3. *Sulphuric acid*, H_2SO_4.		
$[S, O^3]$	103,240	Liquid SO_3 formed from its elements.
$[SO^2, O]$	32,160	Liquid SO_3 formed from SO_2 and O.
$[S^2, O^7, H^2]$	230,500	„ $H_2S_2O_7$ formed from its elements.
$[2SO^3, H^2O]$	24,020	Liquid $H_2S_2O_7$ formed from $2SO_3$ and H_2O.
$[S, O^4, H^2]$	192,920	Liquid H_2SO_4 formed from its elements.
$[S, O^3, H^2O]$	124,560	Formation of liquid H_2SO_4 from the constituents specified.
$[SO^2, O, H^2O]$	53,480	
$[SO^3, H^2O]$	21,320	
$[SO^2, O^2, H^2]$	121,840	
$[S, O^3, Aq]$	142,410	Formation of sulphuric acid in aqueous solution.
$[SO^2, O, Aq]$	71,330	
$[SO^2Aq, O]$	63,630	
$[SO^3, Aq]$	39,170	Heats of solution of the anhydride and the acids, with 1600 formula-weights of H_2O.
$[S^2O^7H^2, Aq]$	54,320	
$[SO^4H^2, Aq]$	17,850	
$[2NaOHAq, SO^3Aq]$	31,380	Heat of neutralisation.

4. *Thiosulphuric acid*, $H_2S_2O_3$.

[S^2, O^2, Aq]	69,470	Formation in aqueous solution.
[S^2, O^3, H^2, Aq]	137,830	
[SO^2, S, Aq]	− 1,610	Formation from sulphurous acid and sulphur.
[SO^{2}Aq, S]	− 9,310	
[SO^{3}Aq, SH^2]	− 9,320	Formation from SH_2 and aqueous sulphuric acid.
[Na^2, S^2, O^3, 5H^{2}O]	265,070	Product, $Na_2S_2O_3.5H_2O$.

5. *Dithionic acid*, $H_2S_2O_6$.

[S^2, O^5, Aq]	211,080	Formation of aqueous solutions from the elements.
[S^2, O^6, H^2, Aq]	279,440	
[2SO^2, O, Aq]	68,920	Formation by oxidation of SO_2 or SO_2Aq.
[2SO^{2}Aq, O]	53,520	
[SO^{3}Aq, SO^{2}Aq]	− 10,110	Formation from SO_3Aq and SO_2Aq.
[K^{2}SO^4, SO^2]	0	Formation of $K_2S_2O_6$ from K_2SO_4 and SO_2.
[K^{2}OAq, S^{2}O^{5}Aq]	27,070	Heat of neutralisation.
[K^2, S^2, O^6]	415,720	Heat of formation of $K_2S_2O_6$.
[K^{2}S^{2}O^6, Aq]	− 13,010	Heat of solution of the same.

6. *Tetrathionic acid*, $H_2S_4O_6$.

[S^4, O^5, Aq]	192,430	Formation of aqueous solutions from the elements.
[S^4, O^6, H^2, Aq]	260,790	
[S^{2}O^{6}H^{2}Aq, S^2]	− 18,650	Formation from dithionic acid and S_2.
[2S^{2}O^{3}H^{2}Aq, O]	53,490	Formation by oxidation of thiosulphuric acid.
[K^2, O^2, S^2, 2SO^2]	255,050	Formation of crystallised $K_2S_4O_6$.

7. *Sulphurous chloride*, S_2Cl_2.

[S^2, Cl^2]	14,260	Direct formation.
[S^{2}Cl^2, S^2]	− 1,660	Heat of solution of sulphur in S_2Cl_2.

8. *Sulphuryl chloride*, SO_2Cl_2.

[S, O^2, Cl^2]	89,780	Formation from the elements.
[SO^2, Cl^2]	18,700	„ „ SO_2 and Cl_2.

SELENION (amorphous).

Reaction	Thermal value	Remarks
1. *Selenion chlorides*, Se_2Cl_2 and $SeCl_4$.		
[Se^2, Cl^2]	22,150	Direct formation.
[Se, Cl^4]	46,160	
[Se^2Cl^2, $3Cl^2$]	70,170	Formation of $SeCl_4$ from Se_2Cl_2.
[$SeCl^4$, Aq]	30,370	Heat of solution of selenion tetrachloride.
2. *Selenious oxide*, SeO_2.		
[Se, O^2]	57,080	Formation of crystallised oxide.
[Se, O^2, Aq]	56,160	„ in aqueous solution.
[SeO^2, Aq]	− 920	Heat of solution.
[Na^2OAq, SeO^2Aq]	27,020	Heat of neutralisation.
3. *Selenic acid*, H_2SeO_4.		
[Se, O^3, Aq]	76,660	Formation from the elements.
[SeO^2, O, Aq]	19,580	„ „ cryst. SeO_2.
[SeO^2Aq, O]	20,500	„ by oxidation of SeO_2Aq.
[Na^2OAq, SeO^3Aq]	30,390	Heat of neutralisation.

TELLURIUM.

Reaction	Thermal value	Remarks
1. *Tellurium tetrachloride*, $TeCl_4$.		
[Te, Cl^4]	77,380.	Direct formation.
[$TeCl^4$, Aq]	20,340	Decomposition by water.
2. *Tellurous acid*, H_2TeO_3.		
[Te, O^2, H^2O]	77,180	Formed from tellurium, oxygen, and water.
3. *Telluric acid*, H_2TeO_4.		
[Te, O^3, Aq]	98,380	Direct formation in aqueous solution.
[$TeO^2.H^2O$, O, Aq]	21,200	Formation by oxidation of $TeO_2.H_2O$.

NITROGEN.

Reaction	Thermal value	Remarks
		1. *Ammonia*, NH_3.
$[N, H^3]$	11,890	Heat of formation.
$[N, H^3, Aq]$	20,320	Formation in aqueous solution.
$[NH^3, Aq]$	8,430	Heat of solution.
$[NH^3, HCl]$	41,900	Formation of the crystallised compounds from the gaseous constituents; e.g. NH_4Cl from NH_3 and HCl.
$[NH^3, HBr]$	45,020	
$[NH^3, HI]$	43,460	
$[NH^3, H^2S]$	22,440	
$[N, H^4, Cl]$	75,790	Formation of the salts from the elements.
$[N, H^4, Br]$	65,350	
$[N, H^4, I]$	49,310	
$[N, H^5, S]$	39,070	
$[N^2, H^4, O^2]$	64,950	
$[N^2, H^4, O^3]$	88,060	
$[NH^3Aq, HClAq]$	12,270	Heats of neutralisation.
$[NH^3Aq, H^2SAq]$	6,190	
		2. *Hydroxylamine*, NOH_3.
$[N, H^3, O, Aq]$	24,290	Formation in aqueous solution.
$[NH^3Aq, O]$	3,970	„ by oxidation of NH_3Aq.
$[N, O, H^4, Cl]$	76,510	„ of cryst. $NH_3O.HCl$ from the elements.
$[NOH^4Cl, Aq]$	− 3,650	Heats of solution of the chloride and sulphate.
$[N^2O^2H^6.H^2SO^4, Aq]$	− 960	
$[NOH^3Aq, HClAq]$	9,260	Heats of neutralisation.
$[2NOH^3Aq, H^2SO^4Aq]$	21,580	
		3. *Nitrous oxide*, N_2O.
$[N^2, O]$	− 17,470	Heat of formation.
$[NO, N]$	+ 3,835	Formed from NO and N.
$[N^2O, 2H^2O]$	− 30,920	Product, $NH_4.NO_3$.
		4. *Nitric oxide*, NO.
$[N, O]$	− 21,575	Heat of formation.
$[N^2O, O]$	− 25,410	Product, 2NO.

5. *Nitrous acid*, HNO_2.

$[N^2, O^3, Aq]$	− 6,820	Formation in aqueous solution.
$[N, O^2, H, Aq]$	+ 30,770	
$[N^2O^2, O, Aq]$	− 36,330	,, from NO.
$[NO, O, H, Aq]$	+ 52,345	
$[N^2, 2H^2O]$	− 71,770	Product, $NH_4.NO_2$.

6. *Nitrogen dioxide*, NO_2.

$[N, O^2]$	− 2,005	Heat of formation.
$[NO, O]$	+ 19,570	Formed from NO and O.
$[NO^2, Aq]$	7,755	Heat of solution.

7. *Nitric acid*, HNO_3.

$[N^2, O^5, Aq]$	29,820	Formation in aqueous solution, by oxidation of N_2, N_2O, N_2O_2 or N_2O_4.
$[N^2O, O^4, Aq]$	47,560	
$[N^2O^2, O^3, Aq]$	72,970	
$[N^2O^4, O, Aq]$	33,830	
$[N, O^3, H]$	41,610	Formation of HNO_3 from the constituents mentioned.
$[NO, O^2, H]$	63,185	
$[NO^2, O, H]$	43,615	
$[N^2O^4, O, H^2O]$	18,770	
$[NO^3H, Aq]$	7,840	Heat of solution.
$[N, O^3, H, Aq]$	49,090	Formation of HNO_3 in aqueous solution.
$[NO, O^2, H, Aq]$	70,665	
$[NO^2, O, H, Aq]$	51,095	
$[NO^2HAq, O]$	18,320	
$[NaOHAq, HNO^3Aq]$	13,680	Heat of neutralisation.

8. *Cyanogen, and Hydrocyanic acid.*

$[C^2, N^2]$	− 65,700	Gaseous products.
$[C, N, H]$	− 27,480	
$[C^2N^2, H^2]$	+ 10,740	Product, 2CNH.

PHOSPHORUS.

1. *Chlorides and Oxychloride.*

Reaction	Thermal value	Remarks
$[P, Cl^3]$	75,300	Direct formation from the elements.
$[P, Cl^5]$	104,990	
$[P, Cl^3, O]$	145,960	
$[PCl^3, Cl^2]$	29,690	Formation from PCl_3.
$[PCl^3, O]$	70,660	
$[PCl^3, Aq]$	65,140	Heats of solution.
$[PCl^5, Aq]$	123,440	
$[POCl^3, Aq]$	72,190	

2. *Hypophosphorous acid*, H_3PO_2.

$[P, O^2, H^3]$	139,970	Crystallised acid.
	137,660	Liquid acid.
$[P, O^2, H^3, Aq]$	139,800	Aqueous solution.
$[PO^2H^3, Aq]$	− 170	Heat of solution of the crystallised acid.
	+ 2,140	Heat of solution of the liquid acid.
$[P^2, O, 3H^2O]$	74,860	Product, crystallised acid.
$[P^2, O, Aq]$	74,520	Aqueous solution.

3. *Phosphorous acid*, H_3PO_3.

$[P, O^3, H^3]$	227,700	Crystallised acid.
	224,630	Liquid acid.
$[P, O^3, H^3, Aq]$	227,570	Aqueous solution.
$[PO^3H^3, Aq]$	− 130	Heat of solution of the crystallised acid.
	+ 2,940	Heat of solution of the liquid acid.
$[P^2, O^3, 3H^2O]$	250,320	Crystallised acid.
$[P^2, O^3, Aq]$	250,060	Aqueous solution.

4. *Phosphoric acid*, H_3PO_4.

$[P, O^4, H^3]$	302,600	Crystallised acid.
	300,080	Liquid acid.
$[P, O^4, H^3, Aq]$	305,290	Aqueous solution.
$[PO^4H^3, Aq]$	2,690	Crystallised acid.
	5,210	Liquid acid.
$[P^2, O^5]$	369,900	Anhydride.
$[P^2, O^5, 3H^2O]$	400,120	Crystallised acid.
$[P^2, O^5, Aq]$	405,500	Aqueous solution.

ARSENIC.

Reaction	Thermal value	Remarks

1. *Arsenious chloride*, $AsCl_3$.

Reaction	Thermal value	Remarks
$[As, Cl^3]$	71,390	Heat of formation.
$[AsCl^3, Aq]$	17,580	Heat of solution.

2. *Arsenious oxide*, As_2O_3.

Reaction	Thermal value	Remarks
$[As^2, O^3]$	154,670	Anhydride.
$[As^2, O^3, Aq]$	147,120	Formation in aqueous solution.
$[As^2O^3, Aq]$	− 7,550	Heat of solution.
$[Na^2OAq, As^2O^3Aq]$	+ 13.780	Heat of neutralisation.

	3. *Arsenic acid*, H_3AsO_4.	
$[As^2, O^5]$	219,380	Anhydride.
$[As^2, O^5, 3H^2O]$	226,180	Solid acid.
$[As^2O^5, 3H^2O]$	6,800	Acid formed from As_2O_5 and $3H_2O$.
$[As^2, O^5, Aq]$	225,380	Aqueous solution.
$[As, O^4, H^3]$	215,630	Crystallised acid.
$[As^2O^3, O^2]$	64,710	Oxidation of arsenious oxide to form arsenic oxide. Measured directly = 64,860 and 78,410.
$[As^2O^3Aq, O^2]$	78,260	
$[As^2O^5, Aq]$	6,000	Heats of solution.
$[AsO^4H^3, Aq]$	− 400	

ANTIMONY.

Reaction	Thermal value	Remarks
	1. *Chlorides.*	
$[Sb, Cl^3]$	91,390	Heats of formation.
$[Sb, Cl^5]$	104,870	
$[SbCl^3, Cl^2]$	13,480	$SbCl_5$ formed from $SbCl_3$.
$[SbCl^3, Aq]$	7,730	Complete decomposition.
	8,910	Formation of $Sb_4O_5Cl_2$.
$[SbCl^5, Aq]$	35,200	Complete decomposition.
	2. *Antimonious acid.*	
$[Sb^2, O^3, 3H^2O]$	167,420	Formation of solid acid $HSbO_2.H_2O$.
$[Sb, O^2, H, H^2O]$	117,890	
	3. *Antimonic acid.*	
$[Sb^2, O^5, 3H^2O]$	228,780	Formation of solid acid $HSbO_3.H_2O$.
$[Sb, O^3, H, H^2O]$	148 570	
$[SbO^3H^3, O]$	30,680	

BISMUTH.

Reaction	Thermal value	Remarks
	1. *Bismuthous chloride and Bismuthous oxychloride*, $BiCl_3$ and BiOCl.	
$[Bi, Cl^3]$	90,630	Heats of formation.
$[Bi, O, Cl, H^2O]$	88,180	
$[BiCl^3, H^2O, Aq]$	7,830	Formation of $BiOCl\,.\,H_2O$.
$[BiCl^3, 3H^2O, Aq]$	− 6,350	" " BiO_3H_3 from $BiCl_3$.
$[BiO^3H^3, HClAq]$	+ 14,180	" " BiOCl from BiO_3H_3.

2. *So-called bismuthic acid*, BiO_3H_3.

$[Bi^2, O^3, 3H^2O]$	137,740	Heats of formation.
$[Bi, O^2, H, H^2O]$	103,050	

Carbon.

Reaction	Thermal value for gaseous products		Remarks
	At constant pressure	At constant volume	
1. Compounds with hydrogen.			
$[C, H^4]$	21,750	21,170	Methane.
$[C^2, H^6]$	28,560	27,400	Ethane.
$[C^2, H^4]$	− 2,710	− 3,290	Ethylene.
$[C^2, H^2]$	− 48,170	− 48,170	Acetylene.
$[C^6, H^6]$	− 1,110	− 2,270	Heat of formation for liquid benzene = + 6090.
$[C^2H^2, H^2]$	+ 45,460	+ 44,880	Product, C_2H_4.
$[C^2H^4, H^2]$	31,270	30,690	„ C_2H_6.
$[C^2H^6, H^2]$	14,940	14,940	„ $2CH_4$.
2. Compounds with chlorine.			
$[C, Cl^4]$	21,030	20,450	For liquid $CCl_4 = 28,230$.
$[C^2, Cl^4]$	− 1,150	− 1,730	„ $C_2Cl_4 = 6000$.
$[C^2Cl^4, Cl^4]$	43,210	42,630	Product, $2CCl_4$.
$[CCl^4, 4H^2]$	88,720	88,720	„ $CH_4 + 4HCl$.
$[CH^4, 4Cl^2]$	87,280	87,280	„ $CCl_4 + 4HCl$.
3. Compounds with oxygen and sulphur.			
$[C, O]$	29,000	29,290	
$[C, O^2]$	96,960	96,960	According to Favre and Silbermann.
$[C, S^2]$	− 26,010	− 25,430	For liquid $CS_2 = -19,610$.
$[C, O, S]$	37,030	37,320	Heats of formation.
$[C, O, Cl^2]$	55,140	54,850	
$[CO, O]$	67,960	67,670	
$[CO, S]$	8,030	8,030	
$[CO, Cl^2]$	26,140	25,560	
4. Compounds with nitrogen.			
$[C^2, N^2]$	− 65,700	− 65,700	
$[C, N, H]$	− 27,480	− 27,480	For liquid $CNH = -21,780$.
$[C^2, N^2, H^2]$	+ 10,740	+ 10,740	Product, 2CNH.
$[C^2H^2, N^2]$	− 6,790	− 6,790	
$[CNH, 3H^2]$	+ 61,120	+ 59,960	Product, $CH_4 + NH_3$.

5. *Oxalic acid and Carbon dioxide.*

Reaction	Thermal value	Remarks
$[C^2, O^4, H^2]$	202,540	Product, dehydrated acid.
$[C^2, O^4, H^2, 2H^2O]$	208,870	,, crystallised acid.
$[C^2O^4H^2, 2H^2O]$	6,330	Formation of the hydrate.
$[C^2O^4H^2, Aq]$	– 2,260	Heats of solution of oxalic acid.
$[C^2O^4H^2 . 2H^2O, Aq]$	– 8,590	
$[CO^2, Aq]$	+ 5,880	Heat of solution of carbon dioxide.
$[C, O^2, Aq]$	102,840	Product, CO_2Aq.
$[CO, O, Aq]$	73,840	
$[2CO, O, Aq]$	73,920	,, C_2O_3Aq.

II. *Heats of formation of compounds of metals according to the investigations of Thomsen*[1].

All the values hold good for a temperature of about 18°C, and for the normal state of the bodies at that temperature.

In tables 1, 2, 3, and 5, column 1 contains the formula, and therefore shews the constituents of the compound; column 2 contains the quantity of heat evolved in the reaction, and column 3 the heat of solution of the product; while the value in column 4, which is the sum of the corresponding values in columns 1 and 2, expresses the quantity of heat evolved supposing the compound to be formed in presence of a large quantity of water.

METALLIC CHLORIDES.

Reaction	Heat of formation of the compound	Heat of solution of the compound	Heat of formation of the compound in aqueous solution
$[K^2, Cl^2]$	211,220	– 8,880	202,340
$[Na^2, Cl^2]$	195,380	– 2,360	193,020
$[Li^2, Cl^2]$	187,620	+ 16,880	204,500
$[Ba, Cl^2]$	194,740	+ 2,070	196,810
$[Ba, Cl_2, 2H^2O]$	201,740	– 4,930	
$[Sr, Cl^2]$	184,550	+ 11,140	195,690
$[Sr, Cl^2, 6H^2O]$	203,190	– 7,500	

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[1] *Thermochemische Untersuchungen*, 3. 505–522.

$[Ca, Cl^2]$	169,820	+ 17,410	187,230
$[Ca, Cl^2, 6H^2O]$	191,980	− 4,340	
$[Mg, Cl^2]$	151,010	+ 35,920	186,930
$[Mg, Cl^2, 6H^2O]$	183,980	+ 2,950	
$[Al^2, Cl^6]$	321,960	+ 153,690	475,650
$[Mn, Cl^2]$	111,990	+ 16,010	128,000
$[Mn, Cl^2, 4H^2O]$	126,460	+ 1,540	
$[Zn, Cl^2]$	97,210	+ 15,630	112,840
$[Cd, Cl^2]$	93,240	+ 3,010	96,250
$[Cd, Cl^2, 2H^2O]$	95,490	+ 760	
$[Fe, Cl^2]$	82,050	+ 17,900	99,950
$[Fe, Cl^2, 4H^2O]$	97,200	+ 2,750	
$[Fe^2, Cl^6]$	192,080	+ 63,360	255,440
$[Co, Cl^2]$	76,480	+ 18,340	94,820
$[Co, Cl^2, 6H^2O]$	97,670	− 2,850	
$[Ni, Cl^2]$	74,530	+ 19,170	93,700
$[Ni, Cl^2, 6H^2O]$	94,860	− 1,160	
$[Cu^2, Cl^2]$	65,750	——	——
$[Cu, Cl^2]$	51,630	+ 11,080	62,710
$[Cu, Cl^2, 2H^2O]$	58,500	+ 4,210	
$[Pb, Cl^2]$	82,770	− 6,800	75,970
$[Hg^2, Cl^2]$	82,550	——	——
$[Hg, Cl^2]$	63,160	− 3,300	59,860
$[Hg, Cl^2, 2KCl, H^2O]$	69,290	− 16,390	52,900
$[Tl^2, Cl^2]$	97,160	− 20,200	76,960
$[Ag^2, Cl^2]$	58,760	——	——
$[Au^2, Cl^2]$	11,620	——	——
$[Au, Cl^3]$	22,820	+ 4,450	27,270
$[Au, Cl^3, 2H^2O]$	28,960	− 1,690	
$[Au, Cl^4, H, 4H^2O]$	76,950	− 5,830	71,120
$[Sn, Cl^2]$	80,790	+ 350	81,140
$[Sn, Cl^2, 2H^2O]$	86,560	− 5,370	
$[Sn, Cl^2, 2KCl, H^2O]$	85,680	− 13,420	72,260
$[Sn, Cl^4]$	127,250	+ 29,920	157,170
$[Sn, Cl^4, 2KCl]$	151,400	− 3,380	148,020
$[Pd, Cl^2, 2KCl]$	52,670	− 13,630	39,040
$[Pd, Cl^4, 2KCl]$	79,060	− 15,000	64,060
$[Pt, Cl^2, 2KCl]$	45,170	− 12,220	32,950
$[Pt, Cl^2, 2AmCl]$	42,550	− 8,480	34,070
$[Pt, Cl^4, 2KCl]$	89,500	− 13,760	75,740
$[Pt, Cl^4, 2NaCl]$	73,720	+ 8,540	82,260
$[Pt, Cl^4, 2NaCl, 6H^2O]$	92,890	− 10,630	
$[Te, Cl^4]$	77,380	+ 20,340	97,720
$[As, Cl^3]$	71,390	+ 17,580	88,970
$[Sb, Cl^3]$	91,390		
$[Sb, Cl^5]$	104,870		
$[Bi, Cl^3]$	90,630		

METALLIC BROMIDES.

The values are calculated for liquid bromine. Reactions for bromine water are 1020 units less than the figures in the table.

Reaction	Heat of formation of the compound	Heat of solution of the compound	Heat of formation of the compound in aqueous solution
$[K^2, Br^2]$	190,620	− 10,160	180,460
$[Na^2, Br^2]$	171,540	− 380	171,160
$[Na^2, Br^2, 4H^2O]$	180,580	− 9,420	
$[Li^2, Br^2]$	——	——	182,620
$[Ba, Br^2]$	169,960	+ 4,980	174,940
$[Ba, Br^2, 2H^2O]$	179,070	− 4,130	
$[Sr, Br^2]$	157,700	+ 16,110	173,810
$[Sr, Br^2, 6H^2O]$	181,010	− 7,200	
$[Ca, Br^2]$	140,850	+ 24,510	165,360
$[Ca, Br^2, 6H^2O]$	166,450	− 1,090	
$[Mg, Br^2]$	——	——	165,050
$[Al^2, Br^6]$	239,440	+ 170,600[1]	410,040
$[Mn, Br^2]$	——	——	106,120
$[Zn, Br^2]$	75,930	+ 15,030	90,960
$[Cd, Br^2]$	75,200	+ 440	75,640
$[Cd, Br^2, 4H^2O]$	82,930	− 7,290	
$[Fe, Br^2]$	——	——	78,070
$[Co, Br^2]$	——	——	72,940
$[Ni, Br^2]$	——	——	71,820
$[Cu^2, Br^2]$	49,970	——	——
$[Cu, Br^2]$	32,580	+ 8,250	40,830
$[Pb, Br^2]$	64,450	− 10,040	54,410
$[Hg^2, Br^2]$	68,290	——	——
$[Hg, Br^2]$	50,550	——	——
$[Hg, Br^2, 2KBr]$	51,780	− 9,750	42,030
$[Tl^2, Br^2]$	82,590	——	——
$[Tl^2, Br^6]$	——	——	112,900
$[Ag^2, Br^2]$	45,400	——	——
$[Au^2, Br^2]$	− 160	——	——
$[Au, Br^3]$	+ 8,850	− 3,760	5,090
$[Au, Br^4, H, 5H^2O]$	52,560	− 11,400	41,160
$[Pt, Br^2, 2KBr]$	32,310	− 10,630	21,680
$[Pt, Br^4, 2KBr]$	59,260	− 12,260	47,000
$[Pt, Br^4, 2NaBr]$	46,790	+ 9,990	56,780
$[Pt, Br^4, 2NaBr, 6H^2O]$	65,330	− 8,550	

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[1] This value is taken from Berthelot's investigations.

METALLIC IODIDES.

The values are calculated for solid iodine.

Reaction	Heat of formation of the compound	Heat of solution of the compound	Heat of formation of the compound in aqueous solution
$[K^2, I^2]$	160,260	− 10,220	150,040
$[Na^2, I^2]$	138,160	+ 2,440	140,600
$[Na^2, I^2, 4H^2O]$	148,620	− 8,020	
$[Li^2, I^2]$	——	——	152,200
$[Ba, I^2, 7H^2O]$	151,370	− 6,850	144,520
$[Sr, I^2]$	——	——	143,460
$[Ca, I^2]$	——	——	134,940
$[Al^2, I^6]$	140,780	+ 178,000	318,780
$[Mg, I^2]$	——	——	134,630
$[Mn, I^2]$	——	——	75,000
$[Zn, I^2]$	49,230	+ 11,310	60,540
$[Cd, I^2]$	48,830	− 960	47,870
$[Fe, I^2]$	——	——	47,650
$[Co, I^2]$	——	——	42,520
$[Ni, I^2]$	——	——	41,400
$[Cu^2, I^2]$	32,520	——	——
$[Pb, I^2]$	39,800	——	——
$[Hg^2, I^2]$	48,440	——	——
$[Hg, I^2]$	34,310	——	——
$[Hg, I^2, 2KI]$	37,350	− 9,810	27,540
$[Tl^2, I^2]$	60,360	——	——
$[Ag^2, I^2]$	27,600	——	——
$[Au^2, I^2]$	− 11,040	——	——
$[Pd, I^2, H^2O]$	+ 18,180	——	——

COMPOUNDS FORMED BY THE ACTION OF AQUEOUS SOLUTIONS OF THE HALOID ACIDS ON HALOID COMPOUNDS OF THE METALS.

If mercury is dissolved in hydrobromic acid, and bromine is added, the result is a solution of $HgBr_2$ $2HBr$, with an evolution of 52,190 units of heat. The same solution may also be formed by dissolving mercuric bromide in hydrobromic acid, but in this case the thermal value is less by the heat of formation of mercuric bromide, for

$$[Hg, Br^2, 2HBrAq] = [Hg, Br^2] + [HgBr^2, 2HBrAq];$$

and since $[Hg, Br^2] = 50{,}550$, it follows that

$$[HgBr^2, 2HBrAq] = 1{,}640.$$

In this way we find the following values :—

$$[HgCl^2, 2HClAq] = -1{,}380$$
$$[HgBr^2, 2HBrAq] = +1{,}640$$
$$[HgI^2, 2HIAq] = 3{,}450$$
$$[AuCl^3, HClAq] = 8{,}980$$
$$[AuBr^3, HBrAq] = 3{,}940.$$

We may also calculate the thermal value of the reaction of an aqueous solution of one of the haloid acids on an aqueous solution of any of the haloid salts in the above table.

Thus required the value of the reaction

$$[Au, Cl^3, HClAq].$$

This reaction, if expanded thermally, may be written thus

$$[Au, Cl^3, HClAq] = [Au, Cl^3] + [AuCl^3, HClAq].$$

Now $[Au, Cl^3] = 22{,}820$ (p. 219)

and $[AuCl^3, HClAq] = 8{,}980.$

$$\text{Sum} = 31{,}800.$$

But the above reaction $[Au, Cl^3, HClAq]$ may also be written as composed of the parts

(1) $[Au, Cl^3, Aq]$, and (2) $[AuCl^3Aq, HClAq]$.

Now $[Au, Cl^3, Aq] = 27{,}270.$

Hence $[AuCl^3Aq, HClAq] = 31{,}800 - 27{,}270$

$$= 4{,}530.$$

The heats of neutralisation of all the acids in the table on p. 223,—regarding, that is to say, $HgCl_2 2HCl$ &c., as definite acids—are equal to that of hydrochloric, hydrobromic, and hydriodic acid respectively, viz. 27,200 gram-units for $2NaOH$. Hence, the heat evolved in the formation of a soluble salt of one of the acids in question is equal to that evolved in formation of the acid itself. Thus

$$[Pt, Cl^2, 2HClAq] = [Pt, Cl^2, 2NaClAq] = [Pt, Cl^2, MgCl^2Aq].$$

This statement holds for the salts of the alkalis, of the alkaline earths, and of the bases of the magnesia series. A further consequence is that platinous chloride, e.g., dissolves with equal development of heat in solutions of hydrochloric acid, calcium chloride, magnesium chloride, or other metallic chlorides.

Reaction	Thermal value
[Hg, Cl^2, 2HClAq]	61,780
[Hg, Br^2, 2HBrAq]	52,190
[Hg, I^2, 2HIAq]	37,760
[Sn, Cl^2, 2HClAq]	81,000
[Sn, Cl^4, 2HClAq]	156,920
[Pd, Cl^2, 2HClAq]	47,920
[Pd, Cl^4, 2HClAq]	72,940?
[Pt, Cl^2, 2HClAq]	41,830
[Pt, Br^2, 2HBrAq]	31,840
[Pt, Cl^4, 2HClAq]	84,620
[Pt, Br^4, 2HBrAq]	57,160
[Au, Cl^3, HClAq]	31,800
[Au, Br^3, HBrAq]	12,790

METALLIC CYANIDES.

See remarks prefixed to preceding tables (p. 218).

Reaction	Heat of formation of the compound	Heat of solution of the compound	Heat of formation of the compound in aqueous solution
[K^2, Cy^2]	130,700	− 6,020	124,680
[Zn, Cy^2]	53,400	——	——
[Cd, Cy^2]	——	——	33,960
[Hg, Cy^2]	18,950	− 2,970	15,986
[Ag^2, Cy^2]	2,790	——	——
[Zn, Cy^2, 2KCyAq]	——	——	62,230
[Cd, Cy^2, 2KCyAq]	——	——	44,750
[Hg, Cy^2, 2KCyAq]	——	——	27,780
[Ag^2, Cy^2, 2KCyAq]	——	——	15,780

METALLIC OXIDES AND HYDROXIDES.

Reaction	Thermal value	Reaction	Thermal value
[K^2, O, Aq]	164,560	[K, O, H, Aq]	116,460
[Na^2, O, Aq]	155,260	[Na, O, H, Aq]	111,810
[Li^2, O, Aq]	166,520	[Li, O, H, Aq]	117,440
[Tl^2, O, Aq]	39,160	[Tl, O, H, Aq]	53,760

$[Ba, O, Aq]$	158,760 ?	$[Ba, O^2, H^2, Aq]$	227,120
$[Sr, O, Aq]$	157,780	$[Sr, O^2, H^2, Aq]$	226,140
$[Ca, O, Aq]$	149,260	$[Ca, O^2, H^2, Aq]$	217,620
$[K^2, O, H^2O]$	137,980	$[Na^2, O]$	99,760 ?
$[Na^2, O, H^2O]$	135,380	$[Tl^2, O]$	42,240
$[Tl^2, O, H^2O]$	45,470	$[Hg^2, O]$	42,200
$[Ba, O, H^2O]$	146,500 ?	$[Cu^2, O]$	40,810
$[Sr, O, H^2O]$	146,140	$[Ag^2, O]$	5,900
$[Ca, O, H^2O]$	146,470	$[Ba, O]$	124,240 ?
$[Mg, O, H^2O]$	148,960	$[Sr, O]$	128,440
$[Mn, O, H^2O]$	94,770	$[Ca, O]$	130,930
$[Zn, O, H^2O]$	82,680	$[Pb, O]$	50,300
$[Sn, O, H^2O]$	68,090	$[Cu, O]$	37,160
$[Fe, O, H^2O]$	68,280	$[Hg, O]$	30,670
$[Cd, O, H^2O]$	65,680	$[As^2, O^3]$	154,590
$[Co, O, H^2O]$	63,400	$[As^2, O^5]$	219,380
$[Ni, O, H^2O]$	60,840		
$[Cu, O, H^2O]$	37,520	$[Al^2, O^3, yH^2O]$	388,920
$[Pd, O, H^2O]$	22,710	$[Fe^2, O^3, yH^2O]$	191,150
$[Pt, O, H^2O]$	17,880	$[Co^2, O^3, yH^2O]$	149,380
		$[Ni^2, O^3, yH^2O]$	120,380
$[Sn, O^2, H^2O]$	133,500	$[Tl^2, O^3, yH^2O]$	86,340
$[Mn, O^2, H^2O]$	116,330	$[Au^2, O^3, yH^2O]$	− 13,190
$[Pd, O^2, H^2O]$	30,430		
$[Te, O^2, H^2O]$	77,180	$[Pb^2, O^3, 3H^2O]$	250,320
$[P^2, O^5, 3H^2O]$	400,120	$[Sb^2, O^3, 3H^2O]$	167,420
$[As^2, O^5, 3H^2O]$	226,180	$[Bi^2, O^3, 3H^2O]$	137,740
$[Sb^2, O^5, 3H^2O]$	228,780		

METALLIC SULPHIDES.

Reaction	Thermal value	Reaction	Thermal value
$[K^2, S, Aq]$	113,300	$[K, S, H, Aq]$	65,140
$[Na^2, S, Aq]$	104,000	$[Na, S, H, Aq]$	60,490
$[Li^2, S, Aq]$	115,260	$[Li, S, H, Aq]$	66,120
$[Ba, S, Aq]$	107,670 ?	$[Ba, S^2, H^2, Aq]$	124,750 ?
$[Sr, S, Aq]$	106,690	$[Sr, S^2, H^2, Aq]$	123,770
$[Ca, S, Aq]$	98,170	$[Ca, S^2, H^2, Aq]$	115,250
		$[Mg, S^2, H^2, Aq]$	114,880
$[Mn, S, yH^2O]$	46,400		
$[Zn, S, yH^2O]$	41,580	$[Tl^2, S]$	21,660
$[Cd, S, yH^2O]$	34,360	$[Pb, S]$	20,430
$[Fe, S, yH^2O]$	23,780	$[Cu^2, S]$	20,270
$[Co, S, yH^2O]$	21,740	$[Hg, S]$	16,890
$[Ni, S, yH^2O]$	19,400	$[Ag^2, S]$	5,340

REACTIONS OF GASEOUS ACIDS ON METALLIC OXIDES.

The products of the reactions represented in the following table are, respectively, metallic chlorides, bromides, iodides, cyanides, or sulphides, and water. In every instance the action of hydriodic acid is attended with the evolution of more heat than the action of hydrobromic acid, and the action of the latter acid is attended with the evolution of more heat than the action of hydrochloric acid. This statement also holds good when aqueous solutions of these acids react on aqueous solutions of metallic salts, provided the haloid compound is insoluble, or nearly insoluble, in the liquid present. Thus, if we precipitate an aqueous solution of a nitrate by means of a solution of hydrochloric, hydrobromic, or hydriodic acid, the evolution of heat, on complete precipitation of the haloid compound, is as follows:

	H_2Cl_2Aq	H_2Br_2Aq	H_2I_2Aq
$Tl_2N_2O_6Aq$	20,350	27,640	35,840
$Ag_2N_2O_6Aq$	31,710	40,220	52,840
$Hg_2N_2O_6Aq$	24,290	31,900	42,470
HgN_2O_6Aq	15,820	25,080	39,260
PbN_2O_6Aq	4,420	7,980	13,750

The heats of neutralisation of the alkaline salts of these three acids being equal to that of nitric acid, the evolution of heat is the same, whether the nitrate is precipitated by a solution of hydrochloric acid, or by a solution of potassium chloride, sodium chloride, magnesium chloride, &c.

Further, the thermal value of the decomposition of the insoluble chlorides and bromides by solutions of compounds of bromine and iodine with the alkaline and various other metals is the difference between the corresponding numbers of the above table; e.g.

$$[Ag^2Cl^2, 2KBrAq] = 40,220 - 31,710 = 8,510$$

$$[Ag^2Cl^2, 2KIAq] = 52,840 - 31,710 = 21,130.$$

Oxide	H_2Cl_2	H_2Br_2	H_2I_2	H_2Cy_2	H_2S
Tl_2O	79,280	91,820	98,560	—	43,040
Ag_2O	77,220	90,980	102,140	54,510	63,060
Hg_2O	64,710	77,570	86,680	—	—
Cu_2O	49,300	60,640	72,150	—	43,080
HgO	56,840	71,350	84,070	45,910	49,830
PbO	56,830	65,630	69,940	—	33,750
CuO	38,830	46,900	—	—	—

METALLIC SULPHATES.

The sulphates specified in the following table are formed from metal, oxygen, and gaseous sulphurous oxide. To find the thermal value of the formation of any sulphate from its elements, add to the given thermal value that of the formation of sulphurous oxide $[S, O^2] = 71{,}080$. The sum of the values contained in the two columns will give the heat of formation in aqueous solution.

Reaction	Thermal value	Heat of solution
$[K^2, O^2, SO^2]$	273,560	- 6,380
$[Na^2, O^2, SO^2]$	257,510	+ 460
$[Na^2, O^2, SO^2, 10H^2O]$	276,730	- 18,760
$[Li^2, O^2, SO^2]$	263,090	+ 6,050
$[Li^2, O^2, SO^2, H^2O]$	265,730	+ 3,410
$[Tl^2, O^2, SO^2]$	149,900	- 8,280
$[Ag^2, O^2, SO^2]$	96,200	- 4,480
$[Pb, O^2, SO^2]$	145,130	——
$[Ba, O^2, SO^2]$	266,990 ?	- 5,580
$[Sr, O^2, SO^2]$	259,820	——
$[Ca, O^2, SO^2]$	247,290	+ 4,440
$[Ca, O^2, SO^2, 2H^2O]$	252,030	- 300
$[Mg, O^2, SO^2]$	231,230	+ 20,280
$[Mg, O^2, SO^2, H^2O]$	238,210	+ 13,300
$[Mg, O^2, SO^2, 7H^2O]$	255,310	- 3,800
$[Mn, O^2, SO^2]$	178,790	+ 13,790
$[Mn, O^2, SO^2, H^2O]$	184,760	+ 7,820
$[Mn, O^2, SO^2, 5H^2O]$	192,540	+ 40
$[Zn, O^2, SO^2]$	158,990	+ 18,430
$[Zn, O^2, SO^2, H^2O]$	167,470	+ 9,950
$[Zn, O^2, SO^2, 7H^2O]$	181,680	- 4,260
$[Cd, O^2, SO^2]$	150,470	+ 10,740
$[Cd, O^2, SO^2, H^2O]$	155,160	+ 6,050
$[Cd, O^2, SO^2, \frac{8}{3}H^2O]$	158,550	+ 2,660
$[Co, O^2, SO^2, 7H^2O]$	162,970	- 3,570
$[Ni, O^2, SO^2, 7H^2O]$	162,530	- 4,250
$[Fe, O^2, SO^2, 7H^2O]$	169,040	- 4,510
$[Cu, O^2, SO^2]$	111,490	+ 15,800
$[Cu, O^2, SO^2, H^2O]$	117,950	+ 9,340
$[Cu, O^2, SO^2, 5H^2O]$	130,040	- 2,750

METALLIC NITRATES.

(1) *Formation of dehydrated nitrates from their elements.*

Reaction	Thermal value
$[K^2, N^2, O^6]$	238,960
$[Na^2, N^2, O^6]$	222,500
$[Li^2, N^2, O^6]$	223,230
$[Tl^2, N^2, O^6]$	116,300
$[Ag^2, N^2, O^6]$	57,480
$[Ba, N^2, O^6]$	226,240 ?
$[Sr, N^2, O^6]$	219,820
$[Ca, N^2, O^6]$	202,630
$[Pb, N^2, O^6]$	105,500

(2) *Formation of nitrates according to the reaction* $[R, O^2, N^2O^4]$.

Reaction	Thermal value	Heat of solution of the salt
$[K^2, O^2, N^2O^4]$	242,970	- 17,040
$[Na^2, O^2, N^2O^4]$	226,510	- 10,060
$[Li^2, O^2, N^2O^4]$	227,240	+ 600
$[Tl^2, O^2, N^2O^4]$	120,310	- 19,940
$[Ag^2, O^2, N^2O^4]$	61,490	- 10,880
$[Ba, O^2, N^2O^4]$	230,250 ?	- 9,400
$[Sr, O^2, N^2O^4]$	223,830	- 4,620
$[Ca, O^2, N^2O^4]$	206,640	+ 3,950
$[Pb, O^2, N^2O^4]$	109,470	- 7,610
$[Sr, O^2, N^2O^4, 4H^2O]$	231,510	- 12,300
$[Ca, O^2, N^2O^4, 4H^2O]$	218,440	- 7,250
$[Cd, O^2, N^2O^4, 4H^2O]$	125,170	- 5,040
$[Mg, O^2, N^2O^4, 6H^2O]$	214,530	- 4,220
$[Mn, O^2, N^2O^4, 6H^2O]$	157,700	- 6,150
$[Zn, O^2, N^2O^4, 6H^2O]$	142,180	- 5,840
$[Ni, O^2, N^2O^4, 6H^2O]$	124,720	- 7,470
$[Co, O^2, N^2O^4, 6H^2O]$	123,330	- 4,960
$[Cu, O^2, N^2O^4, 6H^2O]$	96,950	- 10,710

Formation of metallic sulphates and nitrates in aqueous solutions according to the reaction [R, O, QAq].

R	[R, O, SO^3Aq]	[R, O, N^2O^5Aq]
K^2	195,850	192,100
Na^2	186,640	182,620
Li^2	197,810	194,010
Ba	195,660[1]	187,020 ?
Sr	188,490	185,410
Ca	180,409	177,160
Mg	180,180	176,480
Mn	121,250	117,720
Zn	106,090	102,510
Fe	93,200	89,670
Cd	89,880	86,000
Co	88,070	84,540
Ni	86,950	83,420
Pb	73,800[1]	68,070
Tl^2	70,290	66,540
Cu	55,960	52,410
Hg^2	——	47,990
Hg	——	37,070
Ag^2	20,390	16,780
$Al\frac{2}{3}$	150,630	——
$Fe\frac{2}{3}$	74,990	——

METALLIC DITHIONATES.

Reaction	Thermal value	Heat of solution of the salt
[K^2, O^2, $2SO^2$]	273,560	−13,010
[Na^2, O^2, $2SO^2$]	256,650	− 5,370
[Na^2, O^2, $2SO^2$, $2H^2O$]	262,930	−11,650
[Ag^2, O^2, $2SO^2$, $2H^2O$]	96,090	−10,360
[Ba, O^2, $2SO^2$, $2H^2O$]	262,370 ?	− 6,930
[Sr, O^2, $2SO^2$, $4H^2O$]	263,610	− 9,250
[Ca, O^2, $2SO^2$, $4H^2O$]	253,800	− 7,970
[Pb, O^2, $2SO^2$, $4H^2O$]	145,490	− 8,540
[Cu, O^2, $2SO^2$, $5H^2O$]	126,250	− 4,870
[Mg, O^2, $2SO^2$, $6H^2O$]	248,410	− 2,960
[Mn, O^2, $2SO^2$, $6H^2O$]	188,600	− 1,930
[Zn, O^2, $2SO^2$, $6H^2O$]	173,850	− 2,240
[Ni, O^2, $2SO^2$, $6H^2O$]	154,790	− 2,420

[1] In these reactions insoluble sulphates are formed.

METALLIC CARBONATES.

Thermal value of the formation of the salt according to the formula $[RO, CO^2]$		Thermal value of the formation of the salt according to the formula $[R, O^2, CO]$	
		$[K^2, O^2, CO]$	252,090
		$[Na^2, O^2, CO]$	243,640
$[BaO, CO^2]$	62,220	$[Ba, O^2, CO]$	254,420 ?
$[SrO, CO^2]$	55,770	$[Sr, O^2, CO]$	252,170
$[CaO, CO^2]$	42,520	$[Ca, O^2, CO]$	241,410
		$[Mn, O^2, CO]$	181,840
		$[Cd, O^2, CO]$	152,890
$[PbO, CO^2]$	22,580	$[Pb, O^2, CO]$	140,840
$[Ag^2O, CO^2]$	20,060	$[Ag^2, O^2, CO]$	93,920

Thermal value of the formation of the salt according to the reaction $[R, O, CO^2]$		Thermal value of the formation of the salt from its elements	
$[K^2, O, CO^2]$	184,130	$[K^2, C, O^3]$	281,090
$[Na^2, O, CO^2]$	175,680	$[Na^2, C, O^3]$	272,640
$[Ba, O, CO^2]$	186,460 ?	$[Ba, C, O^3]$	283,420
$[Sr, O, CO^2]$	184,210	$[Sr, C, O^3]$	281,170
$[Ca, O, CO^2]$	173,450	$[Ca, C, O^3]$	270,410
$[Mn, O, CO^2]$	113,880	$[Mn, C, O^3]$	210,840
$[Cd, O, CO^2]$	84,930	$[Cd, C, O^3]$	181,890
$[Pb, O, CO^2]$	72,880	$[Pb, C, O^3]$	169,840
$[Ag^2, O, CO^2]$	25,960	$[Ag^2, C, O^3]$	122,920

METALLIC DOUBLE SALTS.

Column 2 of this table contains the development of heat on direct combination of the solid salts, e.g. dehydrated magnesium sulphate and potassium sulphate combine with a development of 3,300 units of heat. Column 3 contains the heat of solution of the double salt. The sum of the values of columns 2 and 3 gives the development of heat when both salts are simultaneously dissolved in water. If this value is compared with the sum of the heats of solution of the simple salts, the excess of the former over the latter represents the thermal value of the reaction which occurs on mixing the two solutions. Thus the heat of solution of dehydrated magnesium sulphate is 20,280 units, that of potassium sulphate is $-6{,}380$. But since

$$[MgSO^4K^2SO^4, Aq] = 13{,}900$$

it follows that aqueous solutions of the two salts do not react upon each other. The same phenomenon is repeated as regards all the other salts of the first group. But there is often an appreciable development of heat on mixing aqueous solutions of two haloid compounds; e.g.

$$[HgCl^2Aq, K^2Cl^2Aq] = 1,920$$
$$[AuCl^3Aq, HClAq] = 4,530$$
$$[AuBr^3Aq, HBrAq] = 7,700.$$

Reaction	Heat of formation	Heat of solution
$[MgSO^4, K^2SO^4]$	3,300	+ 10,600
$[ZnSO^4, K^2SO^4]$	4,140	+ 7,910
$[CuSO^4, K^2SO^4]$	20	+ 9,400
$[MnSO^4, K^2SO^4]$	990	+ 6,380
$[MgSO^4, K^2SO^4, 6H^2O]$	23,920	- 10,020
$[ZnSO^4, K^2SO^4, 6H^2O]$	23,950	- 11,900
$[CuSO^4, K^2SO^4, 6H^2O]$	22,990	- 13,570
$[MnSO^4, K^2SO^4, 4H^2O]$	13,810	- 6,440
$[HgCl^2, K^2Cl^2, H^2O]$	6,130	- 16,390
$[HgBr^2, K^2Br^2]$	1,230	- 9,750
$[HgI^2, K^2Br^2]$	3,040	- 9,810
$[SnCl^4, K^2Cl^2]$	24,160	- 3,380
$[SnCl^2, K^2Cl^2, H^2O]$	4,890	- 13,420
$[AuCl^3, HCl, 4H^2O]$	32,130	- 5,830
$[AuBr^3, HBr, 5H^2O]$	35,280	- 11,400

DECOMPOSITION OF METALLIC NITRATES BY SULPHURETTED HYDROGEN IN AQUEOUS SOLUTIONS.

A glance at this table will show that the development of heat is positive for those metals that are precipitated by sulphuretted hydrogen in slightly acid solutions, and negative for the other metals. For intermediate metals the reaction (and with it the development of heat) varies with the concentration of the free acid.

R	$[RN^2O^6, SH^2Aq]$
Mn	- 12,260
Fe	- 6,780
Ni	- 4,960
Co	- 3,740
Zn	- 1,870
Cd	+ 7,120
Pb	+ 11,420
Tl_2	+ 14,180
Cu	+ 16,410
Hg	+ 38,870
Ag_2	+ 47,620

III. *Heats of combustion and formation of various compounds, determined by different observers.*

HYDROCARBONS.

Reaction	Thermal value	Remarks
$[CH^4, O^4]$	209,000	Combustion of methane[1].
$[C^2H^4, O^6]$	332,000	,, ,, ethylene[1].
$[C^5H^{10}, O^{15}]$	804,000	,, ,, amylene[1].
$[C^{10}H^{20}, O^{30}]$	1,582,400	,, ,, paramylene[1].
$[C^{11}H^{22}, O^{33}]$	1,734,350	,, ,, endecylene[1].
$[C^{16}H^{32}, O^{48}]$	2,481,500	,, ,, cetene[1].
$[C^{20}H^{40}, O^{60}]$	3,059,840	,, ,, tetramylene[1].
$[C^{10}H^{16}, O^{28}]$	1,475,870	,, ,, liquid turpentine oil[1].
$[C^7H^{16}, O^{22}]$	1,137,450	,, ,, heptane[2].
$[C^7H^{14}, O^{21}]$	1,095,030	,, ,, toluene hexhydride[2].
$[C^6H^6, O^{15}]$	787,950	,, ,, gaseous benzene[3].
$[C^6H^6, O^{15}]$	883,230	,, ,, ,, dipropargyl[3].
$[C^6, H^6]$	−64,800	Formation of gaseous dipropargyl from amorphous carbon[4].
$[C^6, H^6]$	−82,800	Formation of gaseous dipropargyl from diamond carbon[4].
$[C^3H^4, O^8]$	466,500	Combustion of gaseous allylene[5].
$[C^3, H^4]$	−46,500	Formation of gaseous allylene from diamond carbon[5].
$[(C^3H^5)_2, O^{17}]$	904,300	Combustion of gaseous diallyl[6].
$[C^6, H^{10}]$	4,700	Formation of gaseous diallyl from diamond carbon[6].

ALCOHOLS[7] (liquids).

Reaction	Thermal value	Remarks
$[CH^3CH^2CH^2OH, O^9]$	480,310	Combustion of normal propyl alcohol.

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[1] Favre and Silbermann, *Ann. Chim. Phys.* (3). **34.** 427 *et seq.*

[2] Longuinine, *Compt. rend.* **93**, 275.

[3] Thomsen, *Ber.* **15.** 328.

[4] Berthelot and Ogier, *Compt. rend.* **91.** 786.

[5] Berthelot, *Compt. rend.* **90.** 1242 : **91.** 738.

[6] Berthelot and Ogier, *Compt. rend.* **92.** 770.

[7] W. Longuinine, *Compt. rend.* **90**, 1279 ; **91.** 297 ; **92.** 455 and 526.

$[(CH^3)_2CHOH, O^9]$	478,250	Combustion of isopropyl alcohol.
$[(CH^3)_2CHCH_2OH, O^{12}]$	636,700	„ „ primary (fermentation) isobutyl alcohol.
$[(CH^3)_3COH, O^{12}]$	632,820	Combustion of (*solid*) trimethylcarbinol.
$[C^5H^{12}O, O^{15}]$	793,620	Combustion of fermentation amyl-alcohol (probably a mixture).
$[(CH^3)_2C^2H^5COH, O^{15}]$	788,540	Combustion of ethyl dimethylcarbinol.
$[C^3H^5(CH^3)_2COH, O^{17}]$	914,030	Combustion of allyl-dimethyl carbinol.
$[CH^2CHCH^2OH, O^8]$	442,650	Combustion of allyl-alcohol.
$[C^3H^5(C^3H^7)_2COH, O^{29}]$	1,544,990	Combustion of allyl-dipropylcarbinol.
$[C^{10}H^{20}O, O^{29}]$	1,509,160	Combustion of (*solid*) menthol.
$[C^2H^5C^2H^3CHOH, O^{14}]$	753,210	„ „ ethyl-vinyl carbinol.
$[C^8H^{18}O, O^{24}]$	1,262,100	Combustion of caproic alcohol.
$[(C^3H^5)_2CH^3COH, O^{22}]$	1,201,430	„ „ diallyl-methylcarbinol.
$[CH^4O, O^3]$	169,830	Combustion of methylic alcohol[1].
$[C, H^4, O]$	62,000	Formation of liquid methylic alcohol[1].
$[C^2H^6O, O^6]$	330,450	Combustion of ethylic alcohol[1].
$[C^2, H^6, O]$	—	Formation of liquid ethylic alcohol[2].
	Glycols[3].	
$[CH^2OHCH^2OH, O^5]$	283,290	Combustion of (liquid) ethylene glycol.
$[CH^2OHCH^2CH^2OH, O^8]$	431,170	Combustion of (liquid) normal propylene glycol.
$[CH^2OHCHOHCH_3, O^8]$	436,240	Combustion of (liquid) isopropylene glycol.
$[C(CH^3)_2OHC(CH^3)_2OH, O^{17}]$	897,700	Combustion of (*solid*) pinacone (solid).
	—	
$[C^3H^8O^3, O^7]$	392,450	Combustion of glycerine[4].
	—	
$[C^6H^6O, O^{14}]$	737,150	Combustion of phenol[5].

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[1] Favre and Silbermann, *Ann. Chim. Phys.* (3). **34.** 434.

[2] Berthelot, *Compt. rend.* **91.** 738.

[3] W. Longuinine, *Compt. rend.* **90.** 368 : **91.** 299 : **92.** 527.

[4] Id. *loc. cit.* **90.** 367.

[5] Favre and Silbermann, *Ann. Chim. Phys.* (5). **9.** 179.

ALDEHYDES.

Reaction	Thermal value	Remarks
$[C^2H^4O, O^5]$	280,000	Combustion of liquid ethaldehyde with production of liquid water[1].
$[C^2H^4O, O^5]$	275,000	Combustion of gaseous ethaldehyde with production of gaseous water[2].
$[C^2, H^4, O]$	50,500	Formation of gaseous ethaldehyde from diamond carbon[2].
$[C^2, H^4, O]$	56,500	Formation of liquid ethaldehyde from same materials[2].
$[C^2H^5CHO, O^8]$	420,000	Combustion of propaldehyde[3].
$[C^3, H^6, O]$	69,000	Formation of liquid propaldehyde from diamond carbon[3].
$[C^3H^6, O]$	72,500	Formation of liquid propaldehyde from gaseous propylene and oxygen[3].
$[C^3H^8O, O]$	60,300	Oxidation of normal propyl-alcohol to propaldehyde[4].
$[(CH^3)_2CHCH^2CHO, O^{14}]$	742,170	Combustion of liquid valeraldehyde with production of liquid water[5].
$[CH^3(CH^2)_5CHO, O^{20}]$	1,062,600	Combustion of liquid heptaldehyde[6].
$[CH^3CHCHCHO, O^{10}]$	542,300	Combustion of liquid crotonic-aldehyde[7].

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[1] Berthelot, *Ann. Chim. Phys.* (5). **9**. 179.

[2] Berthelot and Ogier, *Compt. rend.* **92**. 773.

[3] Berthelot, *Compt. rend.* **83**. 414.

[4] W. Longuinine, *Compt. rend.* **92**. 457.

[5] Id. *loc. cit.* **92**. 457.

[6] Id. *loc. cit.* **90**. 1282.

[7] Id. *loc. cit.* **100**. 63.

KETONES.

Reaction	Thermal value	Remarks
$[CH^3COCH^3, O^8]$	424,000	Combustion of acetone[1].
$[(C^2H^5)_2CO, O^{14}]$	736,900	Combustion of diethyl ketone[2].
$[(C^3H^7)_2CO, O^{20}]$	1,053,900	,, ,, dipropyl ketone[2].
$[(C^3H^7)_2{}^{\beta}CO, O^{20}]$	1,045,600	,, ,, di-isopropyl ketone[2].
$[CH^3C^6H^{13}CO, O^{23}]$	1,211,800	,, ,, methyl hexyl ketone[2].
$[(CH^3)_2C.CH.CO.CH^3, O^{16}]$	846,100	,, ,, mesityl oxide[3].
$[C^3, H^6, O]$	65,000	Formation of liquid acetone, from diamond carbon[1].
$[C^3H^6, O]$	68,500	Formation of liquid acetone, from gaseous propylene and oxygen[1].

ETHERS AND ETHEREAL SALTS.

Reaction	Thermal value	Remarks
$[(CH^3)_2O, O^6]$	344,200	Combustion of methyl ether[4].
$[C^2, H^6, O]$	50,800	Formation of gaseous methyl ether from diamond, hydrogen, and oxygen[4].
$[(C^2H^5)_2O, O^{12}]$	668,000	Combustion of ethyl ether[5].
$[C^4, H^{10}, O]$	72,000	Formation of liquid ethyl ether[6].
$[(C^5H^{10})_2O, O^{24}]$	1,609,700	Combustion of amyl ether[5].
$[HCO^2CH^3, O^4]$	238,700	,, methyl formate[7].
$[C^2, H^4, O^2]$	94,200	Formation of liquid methyl formate[7].
$[C^2H^5CO^2H, O^7]$	390,600	Combustion of liquid ethyl formate[7].

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[1] Berthelot, *Compt. rend.* **83**. 414.

[2] Id. *loc. cit.* **98**. 94.

[3] Id. *loc. cit.* **100**. 63.

[4] Id. *loc. cit.* **90**. 1243.

[5] Favre and Silbermann, *Ann. Chim. Phys.* (3). **34**. 433.

[6] Berthelot, *Compt. rend.* **91**. 738.

[7] Ogier, *Compt. rend.* **9**. 671.

$[C^3, H^6, O^2]$	70,500	Formation of liquid ethyl formate[1].
$[CH^3CO^2CH^3, O^7]$	395,300	Combustion of methyl acetate[2].
$[CH^3CO^2C^2H^5, O^{10}]$	553,700	„ ethyl acetate[2].
$[C^3H^7CO^2CH^3, O^{13}]$	693,400	„ methyl butyrate[2].
$[C^3H^7CO^2C^2H^5, O^{16}]$	822,500	„ ethyl butyrate[2].
$[C^4H^9CO^2CH^3, O^{16}]$	855,600	„ methyl valerate[2].
$[C^4H^9CO^2C^2H^5, O^{19}]$	1,018,500	„ ethyl valerate[2].
$[CH^3CO^2C^5H^{11}, O^{19}]$	1,036,200	„ amyl acetate[2].
$[C^4H^9CO^2C^5H^{11}, O^{28}]$	1,469,600	„ amyl valerate[2].
$[C^{15}H^{31}CO^2C^{16}H^{33}, O^{94}]$	4,964,100	„ cetyl palmitate[2].
$[CH^2(OCH^3)_2, O^8]$	433,900	„ methylene dimethyl ether (methylal)[3].
$[CH^3CH(OC^2H^5)_2, O^{17}]$	918,600	„ acetal[4].
$[C^3, H^8, O^2]$	124,100	Formation of liquid methylal from diamond carbon[3].
$[CH^3CO^2C^3H^5, O^{12}]$	655,800	Combustion of liquid allyl acetate[5].
$[CO^2C^2H^5.CO^2C^2H^5, O^{13}]$	716,200	Combustion of liquid ethyl oxalate[5].
$[CH^2(CO^2C^2H^5)_2, O^{16}]$	860,630	Combustion of liquid ethyl malonate[5].
$[C^2H^4(CO^2C^2H^5)_2, O^{19}]$	1,007,700	Combustion of liquid ethyl succinate[5].
$[C^2H^4O, O^5]$	307,500	Combustion of liquid ethylene oxide[6].
$[C^2, H^4, O]$	17,700	Formation of ethylene oxide from its elements (carbon as diamond[6]).
$[C^2H^4, O]$	33,000	Formation of ethylene oxide from ethylene and oxygen[6].

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[1] Ogier, *Compt. rend.* **9.** 671.

[2] Favre and Silbermann, *Ann. Chim. Phys.* (3). **34.** 433.

[3] Berthelot and Ogier, *Compt. rend.* **92.** 774.

[4] Longuinine, *Compt. rend.* **100.** 63.

[5] Id. *loc. cit.* **99.** 1118.

[6] Berthelot, *Bull. Soc. Chim.* (2). **39.** 484.

HALOID DERIVATIVES OF HYDROCARBONS.

Combustion and formation of methyl and ethyl haloid compounds.

Reaction	Thermal value	Remarks
$[CH^3Cl, O^3]$	156,500	Combustion of gaseous methyl chloride, with production of H_2O, HCl, and CO_2[1].
$[CH^3Br, O^{3\frac{1}{2}}]$	180,400	Combustion of gaseous methyl bromide, with production of H_2O, Br gas, and CO_2.
$[CH^3I, O^{3\frac{1}{2}}]$	183,300	Combustion of gaseous methyl iodide, with production of H_2O, I gas, and CO_2.
$[C^2H^5Cl, O^6]$	309,500	Combustion of gaseous ethyl chloride, with production of H_2O, HCl, and CO_2.
$[C^2H^5Br, O^{6\frac{1}{2}}]$	329,500	Combustion of gaseous ethyl bromide, with production of H_2O, Br gas, and CO_2.
$[C, H^3, Cl]$	28,500	Formation of gaseous methyl chloride, from diamond carbon.
$[C, H^3, Br]$	17,100	Formation of gaseous methyl bromide, from diamond carbon.
$[C, H^3, I]$	14,200	Formation of gaseous methyl iodide, from diamond carbon.
$[C, H^3, I]$	15,000	Formation of liquid methyl iodide, from diamond carbon, and solid I.
$[C^2, H^5, Cl]$	38,500	Formation of gaseous ethyl chloride, from diamond carbon.
$[C^2, H^5, Cl]$	45,000	Formation of liquid ethyl chloride, from diamond carbon.
$[C^2H^4, HCl]$	31,900	Formation of gaseous ethyl chloride, from C_2H_4 gas and HCl gas.
$[C^2, H^5, Br]$	31,000	Formation of gaseous ethyl bromide, from diamond carbon.
$[C^2, H^5, Br]$	33,700	Formation of liquid ethyl bromide, from diamond, H, and Br liquid.
$[C^2, H^5, I]$	22,800	Formation of gaseous ethyl iodide, from diamond, H, and I gas.
$[C^2, H^5, I]$	23,900	Formation of liquid ethyl iodide, from diamond, H, and I solid[1].

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[1] *These*, and the intermediate data, are from Berthelot, *Compt. rend.* 91. 455; 703.

The following data present the heats of formation of various gaseous haloid compounds by the action of (1) *gaseous halogens on gaseous paraffins*, (2) *gaseous haloid acids on gaseous olefines*, and (3) *gaseous haloid acids on gaseous alcohols.*

Reaction	Thermal value	Remarks
$[C^2H^6, Cl^2]$	54,800	Products, RCl, RBr, or RI, and HCl, HBr, or HI; all gaseous[1].
$[C^2H^6, Br^2]$	38,800	
$[C^2H^6, I^2]$	16,300	
$[CH^4, Cl^2]$	22,000	
$[CH^4, Br^2]$	12,100	
$[CH^4, I^2]$	− 5,100	
$[C^2H^4, HCl]$	31,900	Products, RCl, RBr, or RI; all gaseous[1].
$[C^2H^4, HBr]$	32,900	
$[C^2H^4, HI]$	39,000	
$[C^5H^{10}, HCl]$	16,900	
$[C^5H^{10}, HBr]$	13,200	
$[C^5H^{10}, HI]$	10,600	
$[C^2H^4, HCl]$	38,300	Products, RCl, RBr, or RI; liquid[1].
$[C^2H^4, HBr]$	39,500	
$[C^2H^4, HI]$	46,500	
$[CH^4O, HCl]$	11,900	Products, RCl, RBr, or RI, and H_2O; all gaseous[1].
$[CH^4O, HBr]$	9,000	
$[CH^4O, HI]$	19,500	
$[C^2H^6O, HCl]$	14,800	
$[C^2H^6O, HBr]$	15,800	
$[C^2H^6O, HI]$	21,100	

COMBUSTION AND FORMATION OF METHYLENE AND ETHYLIDENE CHLORIDES[2].

Reaction	Thermal value	Remarks
$[CH^2Cl^2, O^2, Aq]$	141,700	Products, CO_2 and solution of HCl.
$[CH^2Cl^2, O^2]$	106,800	Products, CO_2 and gaseous HCl.
$[CHCl^2CH^3, O^5, Aq]$	302,000	Products, CO_2 and solution of HCl.
$[CHCl^2CH^3, O^5]$	267,100	Products, CO_2 and gaseous HCl.

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[1] Berthelot, *Compt. rend.* **91.** 741.

[2] Berthelot and Ogier, *Compt. rend.* **92.** 771.

$[C, H^2, Cl^2]$	31,200	Product, gaseous CH_2Cl_2: carbon used in form of diamond.
$[C, H^2, Cl^2]$	37,600	Product, liquid CH_2Cl_2: carbon used in form of diamond.
$[C^2, H^4, Cl^2]$	33,900	Product, gaseous $C_2H_4Cl_2$: carbon used in form of diamond.
$[C^2, H^4, Cl^2]$	40,500	Product, liquid $C_2H_4Cl_2$: carbon used in form of diamond.
$[C^2H^2, 2HCl]$	58,000	Product, gaseous $C_2H_4Cl_2$.

THERMAL VALUES OF THE SUBSTITUTION OF HYDROGEN BY CHLORINE IN VARIOUS GASEOUS MOLECULES[1].

Reaction	Thermal value	Remarks
$[CH^4, Cl^2]$	32,000	Products, $CH_3Cl + HCl$; gaseous.
$[CH^3Cl, Cl^2]$	24,000	„ $CH_2Cl_2 + HCl$ „
$[C^2H^6, Cl^2]$	54,000	„ $C_2H_5Cl + HCl$ „
$[C^2H^5Cl, Cl^2]$	17,400	„ $C_2H_4Cl_2 + HCl$ „
$[C^2H^4O, Cl^2]$	39,400	„ $C_2H_3ClO + HCl$ „
$[CNH, Cl^2]$	15,800	„ $CNCl + HCl$ „

COMBUSTION AND FORMATION OF ETHYLAMINES[2].

Reaction	Thermal value	Remarks
$[C^2H^5NH^2, O^{7\frac{1}{2}}]$	409,700	Combustion of gaseous ethylamine and trimethylamine.
$[(CH^3)_3N, O^{10\frac{1}{2}}]$	592,000	
$[C^2, H^7, N]$	19,800	Formation of gaseous ethylamine from diamond carbon.
$[C^2, H^4, NH^3]$	7,600	Formation of gaseous ethylamine from C, H, and NH_3.
$[C^2H^4, NH^3]$	23,000	Formation of gaseous ethylamine from C_2H_4 and NH_3.
$[C^2H^6O, NH^3]$	6,100	Formation of gaseous ethylamine and H_2O gas, from C_2H_6O and NH_3.
$[C^3, H^9, N]$	- 9,500	Formation of gaseous trimethylamine from diamond carbon.
$[C^3, H^6, NH^3]$	2,700	Formation of gaseous trimethylamine from diamond, and NH_3.
$[3CH^3OH, NH^3]$	- 21,900	Formation of gaseous trimethylamine and H_2O gas, from CH_4O and NH_3.

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[1] Berthelot and Ogier, *Compt. rend.* **92.** 771.

[2] Berthelot, Compt. rend. 91. 140.

CARBON ACIDS.

Reaction	Thermal value	Remarks
[CH^2O^2, O]	96,190	Combustion of liquid formic acid[1].
[$C^2H^4O^2$, O^4]	210,300	” ” acetic[1] acid.
[$C^4H^8O^2$, O^{10}]	496,940	” ” butyric[1] acid.
[$(C^3H^7)^\beta CO^2H$, O^{10}]	517,800	” ” isobutyric[2] acid.
[$C^5H^{10}O^2$, O^{13}]	656,780	” ” valeric[1] acid.
[$C^6H^{12}O^2$, O^{16}]	830,210	” ” caproic[3] acid.
[$C^{16}H^{32}O^2$, O^{46}]	2,384,900	” solid palmitic[1] acid.
[$C^{18}H^{36}O^2$, O^{52}]	2,759,300	” ” stearic[1] acid.
[CO^2, $2NH^3$]	37,700	Production of ammonium carbamate at 10^0 and 710[4] mm.

SODIUM ALCOHOLATES[5].

Reaction	Thermal value	Remarks
[$2C^2H^6O$, Na^2O]	34,700	Action of liquid C_2H_6O on solid Na_2O, with production of solid C_2H_5NaO and liquid H_2O.
[C^2H^6O, NaOH]	250	Action of liquid C_2H_6O on solid NaOH, with production of solid C_2H_5NaO and liquid H_2O.
[C^2H^5NaO, $2C^2H^6O$]	8,060	Action of liquid C_2H_6O on solid C_2H_5NaO, with production of solid $C_2H_5NaO.2C_2H_6O$.
[C^2H^5NaO, $3C^2H^6O$]	8,640	Action of liquid C_2H_6O on solid C_2H_5NaO, with production of solid $C_2H_5NaO.3C_2H_6O$.
[$C^2H^5NaO.2C^2H^6O$, C^2H^6O]	580	Action of liquid C_2H_6O on solid $C_2H_5NaO.2C_2H_6O$, with production of solid $C_2H_5NaO.3C_2H_6O$.
[C^2H^5NaO, H^2O]	1,190	Action of liquid H_2O on solid C_2H_5NaO, with production of liquid C_2H_6O and solid NaOH.

[1] Favre and Silbermann, *Ann. Chim. Phys.* (3). **34**. 438.

[2] Longuinine, *Compt. rend.* **100**. 63.

[3] Id. *loc. cit.* **92**. 525.

[4] Lecher, *Wien. Akad. Ber.* (2 abthl.) **78**. 711.

[5] *De Forcrand, Compt. rend.* **97**. 108.

$[C^2H^5NaO.2C^2H^6O, H^2O]$	$-$ 6,820	Action of liquid H_2O on solid $C_2H_5NaO.2C_2H_6O$, with production of liquid C_2H_6O and solid NaOH.
$[C^2H^5NaO.3C^2H^6O, H^2O]$	$-$ 7,440	Action of liquid H_2O on solid $C_2H_5NaO.3C_2H_6O$, with production of liquid C_2H_6O and solid NaOH.

COMBUSTION AND FORMATION OF DIAZOBENZENE NITRATE[1].

Reaction	Thermal value	Remarks
$[C^6H^4N^2.NO^3H, O^{11\frac{1}{2}}]$	782,900	Combustion of diazobenzene nitrate to form $6CO_2$, $2\frac{1}{2}H_2O$, and N_2.
$[C^6, H^5, N^3, O^3]$	$-$ 47,400	Formation of the same compound from its elements.
$[C^6, H^4, N^2, HNO^3]$	$-$ 89,000	Formation of the same compound from C_6, H_4, N_2, and liquid HNO_3.

CHLORAL HYDRATE AND ALCOHOLATE[2].

Reaction	Thermal value	Remarks
$[CCl^3CHO, H^2O]$	12,100	Production of solid compounds.
$[CCl^3CHO, C^2H^6O]$	14,4000	
$[CCl^3CHO, H^2O]$	7,300	Production of liquid compounds near their melting points.
$[CCl^3CHO, C^2H^6O]$	9,800	
$[CCl^3CHO, H^2O]$	6,200	Production of compounds near their boiling points.
$[CCl^3CHO, C^2H^6O]$	8,500	
$[CCl^3CHO, H^2O]$	2,000	Production of gaseous compounds at 760 mm. pressure.
$[CCl^3CHO, C^2H^6O]$	1,600	

Data presenting the heats of combustion of a number of carbon compounds, including sugars, starches, and allied bodies, are given by C. v. Rechenberg in *J. für prakt. Chemie* (2). **22.** 1—45; and 223—250. From these numbers the thermal values of the inversion of sugars, and of various processes of fermentation &c., are calculated.

[1] Berthelot and Vieille, *Compt. rend.* **92.** 1076.

[2] Berthelot, *Compt. rend.* **92.** 831.

The heats of combustion of various sugars, starches, fats, and other compounds of animal and vegetable origin, are given by Stohmann in the same Journal (2). **31**. 273.

The heats of combustion of a few organic bases are given by Ramsay in C. S. Journal for **1879**. 696 *et seq.*

METALLIC SULPHIDES.

Sulphides of sodium and potassium[1].

Reaction	Thermal value	Remarks
$[Na^2, S]$	88,200	Production of solid Na_2S from the solid elements.
$[Na^2S, 5H^2O]$	14,450	Production of solid Na_2S5H_2O from solid constituents.
$[Na^2S, 9H^2O]$	18,850	Production of solid Na_2S9H_2O from solid constituents.
$[Na^2S5H^2O, 4H^2O]$	4,400	Production of solid Na_2S9H_2O from solid constituents.
$[Na^2, S^2, H^2]$	111,400	Production of solid Na_2SH_2S from H_2, and solid Na_2 and S_2.
$[Na^2S, H^2S]$	18,600	Production of solid Na_2SH_2S from solid Na_2S and gaseous H_2S.
$[Na^2OH^2O, 2H^2S]$	16,300	Production of solid Na_2SH_2S and gaseous H_2O from solid Na_2OH_2O.
$[Na^2SH^2S, 4H^2O]$	6,000	Production of solid $Na_2SH_2S4H_2O$ and gaseous $2H_2S$ from solid constituents.
$[K^2, S]$	104,200 (?)	Production of solid K_2S from the solid elements.
$[K^2, S^2, H^2]$	128,000	Production of solid K_2SH_2S from H_2, and solid K_2 and S_2.
$[K^2S, H^2S]$	19,000 (?)	Production of solid K_2SH_2S from solid K_2S and gaseous H_2S.
$[K^2OH^2O, 2H^2S]$	28,900	Production of solid K_2SH_2S and gaseous H_2O from solid K_2OH_2O and gaseous H_2S.
$[K^2SH^2S, H^2O]$	$-1,200$	Production of solid $K_2SH_2SH_2O$ from solid constituents.
$[K^2SH^2S, H^2O]$	200	Production of solid $K_2SH_2SH_2O$ from solid K_2SH_2S and liquid H_2O.
$[Fe, S]$	25,000	Solid FeS from solid elements[2]

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[1] Sabatier, *Compt. rend.* **89**. 43.

[2] Müllenhoff, *Ber.* **18**. 1365.

Polysulphides of the alkali metals[1].

[K^2, S^4]	117,800	Production of solution of K_2S_4 from K_2 and solid S_4.
[K^2, S^4]	116,600	Production of solid K_2S_4 from K_2 and solid S_4.
[K^2S, S^3]	5,200	Production of solution of K_2S_4 from solution of K_2S and solid S_3
[K^2S, S^3]	12,400	Production of solid K_2S_4 from solid K_2S and solid S_3.
[K^2S^4, $\frac{1}{2}H^2O$]	2,650	Production of solid $K_2S_4\frac{1}{2}H_2O$ from solid constituents.
[K^2S^4, $2H^2O$]	5,750	Production of solid $K_2S_42H_2O$ from solid constituents.
[$K^2S^4\frac{1}{2}H^2O$, $\frac{3}{2}H^2O$]	3,100	Production of solid $K_2S_42H_2O$ from solid constituents.
[Na^2, S^4]	108,200	Production of solution of Na_2S_4 from solid elements.
[Na^2, S^3]	106,400	Production of solution of Na_2S_3 from solid elements.
[Na^2, S^2]	104,200	Production of solution of Na_2S_2 from solid elements.
[Na^2, S^4]	98,400	Production of solid Na_2S_4 from solid elements.
[Na^2S, S^3]	10,200	Production of solid Na_2S_4 from solid Na_2S and solid S_3.
[Na^2S, S^3]	5,000	Production of solution of Na_2S_4 from solution of Na_2S and solid S_3.
[Na^2S, S^2]	3,200	Production of solution of Na_2S_3 from solution of Na_2S and solid S_2.
[Na^2S, S]	1,400	Production of solution of Na_2S_2 from solution of Na_2S and solid S.

Ammonium polysulphides[2].

[N, H^4, S^2]	34,500	Production of solid NH_4S_2 from N, H_4, and solid S_2.
[N, H^4, S^4]	34,800	Production of solid NH_4S_4 from N, H_4, and solid S_4.
[N, H^4, S^2]	30,400	Production of solution of NH_4S_2 from N, H_4, and solid S_2.
[NH^3, $\frac{1}{2}H^2S$, $S^{1\frac{1}{2}}$]	20,200	Production of solid NH_4S_2 from gaseous NH_3, $\frac{1}{2}H_2S$, and solid $S_{\frac{3}{2}}$.
[NH^3, $\frac{1}{2}H^2S$, $S^{3\frac{1}{2}}$]	20,300	Production of solid NH_4S_4 from gaseous NH_3, $\frac{1}{2}H_2S$, and solid $S_{\frac{7}{2}}$.

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[1] Sabatier, *Compt. rend.* **90. 1557.**

[2] Id. *loc. cit.* **91.** 53.

Hydrogen persulphide[1].

$[H^2S, S^{n-1}]$	$-2,650$	Production of solid H_2S_n (*n* varies from 6 to 10).
$[H^2, S^n]$	-350	Production of solid H_2S_n (*n* varies from 6 to 10).

COMPOUNDS OF PH_3 AND NH_3[2].

Reaction	Thermal value	Remarks
$[PH^4Br, Aq]$	$-3,030$	Production of gaseous PH_3 and solution of HBr.
$[PH^4I, Aq]$	$-4,770$	Production of gaseous PH_3 and solution of HI.
$[NH^3, HCl]$	42,500	Production of solid NH_4X or PH_4X, from gaseous NH_3 or PH_3 and HX.
$[NH^3, HBr]$	45,600	
$[NH^3, HI]$	44,200	
$[PH^3, HBr]$	23,000	
$[PH^3, HI]$	24,100	
$[N, H^4, Br]$	81,700	Production of solid NH_4Br from gaseous N, H_4, and liquid Br.
$[N, H^4, I]$	65,100	Production of solid NH_4I from gaseous N, H_4, and solid I.
$[P, H^4, Br]$	44,100	Production of solid PH_4Br from H_4, solid P and liquid Br.
$[P, H^4, I]$	29,500	Production of solid PH_4I from H_4, solid P, and solid I.

COMPOUNDS OF AMMONIA WITH METALLIC CHLORIDES[3].

Reaction	Thermal value	Remarks
$\frac{1}{3}[AgCl, 3NH^3]$	10,500	Production of solid compounds from gaseous NH_3 and solid metallic chloride.
$\frac{1}{3}[2AgCl, 3NH^3]$	11,600	
$\frac{1}{2}[ZnCl^2, 2NH^3]$	22,100	
$\frac{1}{4}[ZnCl^2, 4NH^3]$	17,000	
$\frac{1}{6}[ZnCl^2, 6NH^3]$	15,000	
$\frac{1}{2}[CaCl^2, 2NH^3]$	14,000	
$\frac{1}{4}[CaCl^2, 4NH^3]$	12,200	
$\frac{1}{8}[CaCl^2, 8NH^3]$	11,000	

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[1] Sabatier, *Compt. rend.* **91.** 54.

[2] Ogier, *Compt. rend.* **89.** 705.

[3] Isambert, *Compt. rend.* **86.** 968.

VARIOUS DOUBLE METALLIC SALTS.

Reaction	Thermal value	Remarks
$[CdCl^2, 2HCl, 7H^2O]$	40,200	Production of compounds of metallic haloid salt haloid acid and water, from solid haloid salt, gaseous acid, and liquid water[1].
$[PbI^2, HI, 5H^2O]$	23,300	
$[3AgI, HI, 7H^2O]$	21,600	
$[CuCl^2, 3CuO, 4H^2O]$	23,000	Production of solid compounds from solid copper chloride and oxide and liquid water[2].
$[CuCl^2, 3CuO]$	1,200	
$[CaCl^2, 3CaO, 16H^2O]$	92,000	Production of solid compounds from solid calcium chloride and oxide and liquid water[3].
$[CaCl^2, 3CaO, 3H^2O]$	57,700	
$[CaCl^2, 3CaO, 16H^2O]$	69,100	Production of solid compounds from solid constituents[4].
$[CaCl^2, 3CaO, 3H^2O]$	53,400	
$[CaCl^2 3CaO, 3H^2O]$	47,200	
$[CaCl^2 3CaO, 16H^2O]$	60,900	
$[CaCl^2 3CaO 3H^2O, 13H^2O]$	15,800	
$[2KIPbI^2, 2H^2O]$	1,760	Production of solid compounds from solid constituents[5].
$[2KI, PbI^2]$	840	
$[4KI 3PbI^2, 6H^2O]$	3,800	
$[4KI, 3PbI^2]$	- 100	
$[PbO, PbCl^2]$	6,520	Production of solid compounds from solid constituents[6].
$[2PbO, PbCl^2]$	9,240	
$[3PbO, PbCl^2]$	10,600	
$[PbO, PbBr^2]$	4,000	
$[2PbO, PbBr^2]$	6,060	
$[3PbO, PbBr^2]$	8,400	

[1] Berthelot, *Compt. rend.* **91**. 1024.

[2] Id. *loc. cit.* **91**. 451.

[3] André, *Compt. rend.* **92**. 1453.

[4] Id. *loc. cit.*

[5] Berthelot, *Compt. rend.* **95**. 952.

[6] André, *Compt. rend.* **97**. 1302.

CYANIDES AND DOUBLE CYANIDES[1].

(In each case the carbon was used in the form of diamond.)

action	Remarks regarding constituents	Product	Thermal value according as product is			
			gaseous	liquid	solid	in solution
$N^2]$		C_2N_2	-74,600	—	—	- 69,800
$, H]$		CNH	-29,500	-23,800	—	- 23,400
H]		CNH	7,800	13,500	—	—
Aq,H]	solution of CN	CNH	—	—	—	10,500
, Cl]		CNCl	-35,700	-27,800		
Cl]	gaseous CN	CNCl	1,600	9,900		
, I]	solid I	CNI	—	—	- 38,500	- 41,300
I]	gaseous CN, gaseous I	CNI	—	—	4,200	—
I]	gaseous CN, solid I	CNI	—	—	- 1,200	—
$^2, H^4]$		$CNNH_4$	—	—	3,200	1,200
$N, H^4]$	gaseous CN	$CNNH_4$	—	—	40,500	- 36,100
$H, NH^3]$	gaseous CHN and NH_3	$CNNH_4$	—	—	20,500	—
HAq, $NH^3Aq]$	solutions of CNH and NH_3	$CNNH_4$	—	—	—	- 1,300
, K]		CNK	—	—	30,300	27,400
K]	gaseous CN	CNK	—	—	67,600	64,700
HAq, $K^2OAq]$	solutions of HCN and $\frac{1}{2}K_2O$	CNK	—	—	—	3,000
Na]	gaseous CN	CNNa	—	—	—	60,100
NAq, $a^2OAq]$	solutions of HCN & $\frac{1}{2}Na_2O$	CNNa	—	—	—	2,900
$, \frac{1}{2}Hg]$		$CNHg\frac{1}{2}$	—	—	- 25,600	- 27,100
$\frac{1}{2}Hg]$	gaseous CN and liquid $\frac{1}{2}Hg$	$CNHg\frac{1}{2}$	—	—	11,700	10,200
$\frac{1}{2}Hg]$	gaseous CN and gaseous $\frac{1}{2}Hg$	$CNHg\frac{1}{2}$	—	—	19,400	17,900
NAq, HgOAq]	solutions of HCN & $\frac{1}{2}HgO$	$CNHg\frac{1}{2}$	—	—	—	15,500
, Ag]		CNAg	—	—	- 34,000	—
Ag]		CNAg	—	—	3,300	—
NAq, $\frac{1}{2}Ag^2O]$	solution of HCN, and precipitated $\frac{1}{2}Ag_2O$	CNAg	—	—	—	20,900

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[1] Berthelot, *Compt. rend.* **91.** 82. Compare Thomsen's numbers given in bles on pp. 217 and 223.

$[Fe^{\frac{1}{2}}, H^2, 3CN]$		$(CN)_3Fe_{\frac{1}{2}}H_2$	—	—	—	53,600
$[3HCNAq, \frac{1}{2}FeO]$	precipitated $\frac{1}{2}FeO$	$(CN)_3Fe_{\frac{1}{2}}H_2$	—	—	—	12,300
$[Fe\frac{1}{2}, K^2, 3CN]$		$(CN)_3Fe_{\frac{1}{2}}K_2$	—	—	183,600	186,300 (dissolved in KCN)
$[3HCNAq, K^2OAq, \frac{1}{2}FeO]$	precipitated $\frac{1}{2}FeO$	$(CN)_3Fe_{\frac{1}{2}}K_2$	—	—	—	39,300
$[Fe^{3\frac{1}{2}}, 9CN]$		$(CN)_9Fe_{\frac{7}{2}}$	—	—	278,000	—
$[9HCNAq, \frac{3}{2}FeO, Fe^2O^3]$	precipitated oxides of iron	$(CN)_9Fe_{\frac{7}{2}}$	—	—	24,900	—
$[KCN, CNHg^{\frac{1}{2}}]$		$CNHg_{\frac{1}{2}}KCN$	—	—	8,300	—
$[KCN, AgCN]$		$KCN\,AgCN$	—	—	11,200	—

OXYCYANIDES[1].

Reaction	Thermal value	Remarks
$[Pb, (CN)_2, 2PbO, H^2O]$	17,800	Production of solid $2PbOPb(CN)_2H_2O$ from gaseous $(CN)_2$ and other constituents as solids.
$[2Cd(CN)^2, CdO, 5H^2O]$	22,800	Production of solid $2Cd(CN)_2CdO5H_2O$ from solid constituents.
$[HgO, Hg(CN)^2]$	2,400	Production of solid $HgOHg(CN)_2$ from solid constituents.
$[HgO, 3Hg(CN)^2]$	9,800	Production of solid $HgO3Hg(CN)_2$ from solid constituents.

CYANATES[2].

Reaction	Thermal value	Remarks
[C, N, K, O]	102,300	Production of solid KCNO.
[C, N, K, O, Aq]	97,100	Production of solution of KCNO.
[CNK, O]	72,000	Production of solid KCNO.
[CNK, O, Aq]	69,700	Production of solution of KCNO.

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[1] Joannis, *Compt. rend.* **93**. 271.

[2] Berthelot, *Compt. rend.* **91**. 82.

FLUORIDES[1].

Reaction	Thermal value	Remarks
$[NH^3Aq, HFAq]$	15,200	Production of solution of NH_4F.
$[NH^3, HF]$	30,100	„ „ solid NH_4F from gaseous constituents.
$[BaOAq, 2HFAq]$	34,800	Production of solution of BaF_2.
$[BaH^2O^2, 2HF]$	71,400	„ of solid $BaF_2(+2H_2O)$ from solid BaH_2O_2 and gaseous 2HF.
$[SrOAq, 2HFAq]$	35,800	Production of solution of SrF_2.
$[SrH^2O^2, 2HF]$	71,800	„ of solid $SrF_2(+2H_2O)$ from solid SrH_2O_2 and gaseous 2HF.
$[CaOAq, 2HFAq]$	37,200	Production of solution of CaF_2.
$[CaH^2O^2, 2HF]$	66,600	„ of solid $CaF_2(+2H_2O)$ from solid CaH_2O_2 and gaseous 2HF.
[NaOH, HF]	39,900	Production of solid NaF $(+H_2O)$ from solid NaOH and gaseous HF.
[NaF, HF]	17,100	Production of solid $NaHF_2$ from solid NaF and gaseous HF.
$[MgO^2H^2, 2HFAq]$	30,400	Production of solution of MgF_2.
$[PbO^2H^2, 2HFAq]$	22,200	„ „ solid PbF_2.

SILICOFLUORIDES[2].

Reaction	Thermal value	Remarks
$[SiF^4, Aq]$	22,200	Decomposition of SiF_4 into H_2SiF_6 and SiO_2.
$[SiF^4, 2HFAq]$	17,000	Formation of H_2SiF_6 in solution.
$[3SiF^4, 4KOHAq]$	165,800	Production of $2K_2SiF_6+H_4SiO_4$.
$[SiF^4, 4NaOHAq]$	65,400	„ „ $4NaFAq+H_4SiO_4$.
$[SiF^4, 4NH^3Aq]$	59,500	„ „ $4NH_4FAq+H_4SiO_4$.
$[SiF^4, 4LiOHAq]$	69,200	„ „ $4LiF+H_4SiO_4$.
$[SiF^4, 2KFAq]$	45,600	„ „ K_2SiF_6.
$[SiF^4, 2NaFAq]$	36,600	„ „ Na_2SiF_6.
$[SiF^4, 2LiFAq]$	27,000	„ „ Li_2SiF_6Aq.
$[SiF^4, 2NH^4FAq]$	31,200	„ „ $(NH_4)_2SiF_6Aq$.
$[Si, K^2, F^6]$	52,800	„ „ solid salts.
$[Si, Na^2, F^6]$	35,400	
$[Si, Li^2, F^6]$	25,200	

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[1] Guntz, *Compt. rend.* **97**. 1483, 1558; **98**. 816.

[2] *Truchot, Compt. rend.* **98**. 821, 1330.

$[Si, H^4]$	24,800	Formation of silicon hydride[1].
$[SiH^4, O^4]$	324,300	Production of $SiO_2 + 2H_2O$[1].

COMPOUNDS OF THE HALOGENS[2].

Reaction	Thermal value	Remarks
$[I, Cl]$	6,700	Formation of solid ICl from gaseous Cl and solid I.
$[I, Cl]$	12,100 at 0°	Formation of solid ICl from gaseous Cl and gaseous I.
$[I, Cl^3]$	16,300	Formation of solid ICl_3 from gaseous Cl_3 and solid I.
$[I, Cl^3]$	21,700	Formation of solid ICl_3 from gaseous Cl_3 and gaseous I.
$[ICl, Cl^2]$	9,500	Formation of solid ICl_3 from gaseous Cl_2 and solid ICl.
$[I, Br]$	2,500	Formation of solid IBr from liquid Br and solid I.
$[I, Br]$	2,300	Formation of solid IBr from solid Br and solid I.
$[Br, Cl]$	600	Formation of liquid (?) BrCl from gaseous Cl and liquid Br.
$[Br, Cl]$	4,600	Formation of liquid (?) BrCl from gaseous Cl and gaseous Br.
$[KI, I^2]$	0	Formation of solid KI_3 from solid KI and solid I_2.
$[KI, I^2]$	10,800 at 0°	Formation of solid KI_3 from solid KI and gaseous I_2.
$[KIAq, I^2]$	10,200	Formation of solution of KI_3 from solution of KI and gaseous I_2.
$[KBr, Br^2]$	2,900	Formation of solid KBr_3 from solid KBr and liquid Br_2.
$[KBr, Br^2]$	2,700	Formation of solid KBr_3 from solid KBr and solid Br_2.
$[KBr, Br^2]$	10,900 at 0°	Formation of solid KBr_3 from solid KBr and gaseous Br_2.
$[KBrAq, Br^2]$	11,500	Formation of solution of KBr_3 from concentrated solution of KBr and gaseous Br_2.

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[1] Ogier, *Compt. rend.* **88**. 911.

[2] Berthelot, *Compt. rend.* **90**. 841: **91**. 195, 706.

OXYACIDS OF THE HALOGENS[1].

Reaction	Thermal value	Remarks
$[Cl^2, O^5, H^2O, Aq]$	– 24,000	Formation of dilute solution of $2HClO_3$.
$[Cl^2, O^6, H^2, Aq]$	45,000	Formation of dilute solution of $2HClO_3$.
$[Cl, O^3, K]$	94,600	Formation of solid $KClO_3$.
$[Cl, O^3, Na]$	85,400	Formation of solid $NaClO_3$.
$[Cl, O^4, H]$	19,100	Formation of liquid $HClO_4$.
$[Cl, O^4, H, Aq]$	39,350	Formation of dilute solution of $HClO_4$.
$[Cl, O^4, K]$	112,500	Formation of solid $KClO_4$.
$[Cl, O^4, K, Aq]$	100,400	Formation of dilute solution of $KClO_4$.
$[Cl, O^4, Na]$	100,200	Formation of solid $NaClO_4$.
$[Cl, O^4, Na, Aq]$	96,700	Formation of dilute solution of $NaClO_4$.
$[Cl, O^4, H^4, N]$	79,700	Formation of solid NH_4ClO_4.
$[I^2, O^5, Aq]$	45,200	Formation of solution of $2HIO_3$ from solid I_2 &c.
$[I^2, O^6, H^2, Aq]$	114,200	Formation of solution of $2HIO_3$ from solid I_2 &c.
$[I^2, O^6, H^2]$	119,600	Formation of solid $2HIO_3$.

AMALGAMS[2].

Reaction	Thermal value	Product
$[Na, Hg]$	10,300	HgNa.
$[Na, Hg^6]$	21,600	Hg_6Na crystallised.
$[K, Hg^{\frac{5}{2}}]$	20,300	$Hg_{\frac{5}{2}}K$.
$[K, Hg^{12}]$	34,200	$Hg_{12}K$ crystallised.

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[1] Berthelot, *Ann. Chim. Phys.* (5). **10.** 379 *et seq.*: *Compt. rend.* **84.** 734: **93.** 244 and 290. Compare Thomsen's number as given in tables on pp. 207, 208, 209.

[2] Berthelot, *Compt. rend.* **88.** 1110, 1337.

APPENDIX II.

DATA RELATING TO ALLOTROPIC AND ISOMERIC CHANGES.

OZONE TO OXYGEN.

$[2Oz = 3O^2]$ i.e. change of 96 grams of ozone into 96 grams of oxygen
59,200[1].
68,000[2].

COMBUSTION OF SULPHUR.

$[S, O^2]$[3].

Thermal value	Remarks
70,936	Sulphur melted 7 years before the combustion.
70,840	Sulphur heated to softening point 3 months before the combustion.
71,225	Sulphur crystallised from CS_2.
71,350	Sulphur crystallised from water saturated with H_2S.
71,070	Sulphur crystals from Sicily.
72,330	Sulphur melted after crystallising.
71,970	Native opaque sulphur.
72,790	" " "
74,790	The same but containing some reddish crystals.
71,080	Rhombic sulphur[4].
71,720	Monoclinic sulphur[4].
69,260	Rhombic or monoclinic sulphur[5].

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[1] Berthelot, *Compt. rend.* **90**. 331.

[2] van der Meulen, *Ber.* **8**. 1853.

[3] Favre and Silbermann, *Ann. Chim. Phys.* (3). **34**. 447.

[4] Thomsen, *Ber.* **13**. 961.

[5] Berthelot, *Compt. rend.* **90**. 1445.

COMBUSTION OF PHOSPHORUS.

$[P^2, O^5.]$

Thermal value	Remarks
369,900	Ordinary yellow phosphorus[1].
326,860	Red phosphorus produced by heating ordinary to 580°. Sp. Gr. = 2·34[2].
362,820	Ordinary red phosphorus[2].
345,340	Red phosphorus produced by heating ordinary to 360°. Sp. Gr. = 2·19[2].

COMBUSTION OF CARBON.

$[C, O^2.]$

Thermal value	Remarks
96,960	Amorphous carbon[3].
93,350	Diamond[4].
93,560	Native graphite[4].

COMBUSTION OF SILICON.

$[Si, O^2]$.

Thermal value	Remarks
219,240	Amorphous silicon[5]
211,120	Crystallised silicon[5].

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[1] Thomsen, *Thermochemische Untersuchungen*, **1**. 409.

[2] Troost and Hautefeuille, *Compt. rend.* **78**. 748.

[3] Thomsen, *loc. cit.*, **1**. 411.

[4] Favre and Silbermann, *Ann. Chim. Phys.* (3). 34. 414 ; 423—5.

[5] Troost and Hautefeuille, *Compt. rend.* **70**. 252.

COMBUSTION OF ISOMERIC CARBON COMPOUNDS.

Reaction	Thermal value	Remarks
$[C^6H^6, O^{15}]$	787,950	Combustion of gaseous benzene[1].
$[C^6H^6, O^{15}]$	883,230	Combustion of gaseous dipropargyl[1].
$[CH^3CH^2OH, O^6]$	330,450	Combustion of ethylic alcohol[2].
$[(CH^3)_2O, O^6]$	344,200	Combustion of methyl ether[3].
$[CH^3CH^2CH^2OH, O^9]$	480,310	„ „ primary propyl alcohol[4].
$[(CH^3)_2CHOH, O^9]$	478,250	Combustion of isopropyl alcohol[4].
$[(CH^3)_2CHCH^2OH, O^{12}]$	636,700	Combustion of primary isobutyl alcohol[4].
$[(CH^3)_3COH, O^{12}]$	632,820	Combustion of (*solid*) trimethyl carbinol[4].
$[(C^2H^5)_2O, O^{12}]$	668,000	Combustion of ethyl ether[2].
$[C^5H^{12}O, O^{15}]$	793,620	„ „ fermentation amyl alcohol[4] (probably a mixture).
$[(CH^3)_2C^2H^5COH, O^{15}]$	788,540	Combustion of ethyldimethyl carbinol[4].
$[CH^2CHCH^2OH, O^8]$	442,650	Combustion of allyl alcohol[4].
$[CH^3COCH^3, O^8]$	424,000	„ „ acetone[5].
$[C^2H^5CHO, O^8]$	420,000	„ of propaldehyde[5].
$[C^3H^5(C^3H^7)_2COH, O^{29}]$	1,544,990	„ „ allyl dipropyl carbinol[4].
$[C^{10}H^{20}O, O^{29}]$	1,509,160	Combustion of (*solid*) menthol[4].
$[C^2H^5C^2H^3CHOH, O^{14}]$	733,210	Combustion of ethyl vinylcarbinol[4]
$[(CH^3)_2CHCH^2CHO, O^{14}]$	742,170	Combustion of valeraldehyde[4].
$[(C^2H^5)_2CO, O^{14}]$	736,900	Combustion of diethylketone[6].

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[1] Thomsen, *Ber.* **15**. 328.
[2] Favre and Silbermann, *Ann. Chim. Phys.* (3) **34**. 433.
[3] Berthelot, *Compt. rend.* **90**. 1243.
[4] Longuinine, *Compt. rend.* **90**. 1279 : **91**. 297 : **92**. 455; 526.
[5] Berthelot, *Compt. rend.* **83**. 414.
[6] Longuinine, *Compt. rend.* **98**. 94.

$[CH^2OHCH^2CH^2OH, O^8]$	431,170	Combustion of propylene glycol[1].
$[CH^2OHCH^3CHOH, O^8]$	436,240	Combustion of isopropylene glycol[1].
$[CH^2(OCH^3)_2, O^8]$	433,900	Combustion of methylal[3].
$[C(CH^3)_2OHC(CH^3)_2OH, O^{17}]$	897,700	„ „ pinacone[1].
$[CH^3CH(OC^2H^5)_2, O^{17}]$	918,600	„ „ acetal[4].
$[CH^3(CH^2)_5CHO, O^{20}]$	1,062,600	„ „ heptaldehyde[1].
$[(C^3H^7)_2CO, O^{20}]$	1,053,900	Combustion of dipropylketone[2].
$[(C^3H^7)^{\beta}_2CO, O^{20}]$	1,045,600	Combustion of di-isopropylketone[2].
$[CH^3CO^2H, O^4]$	210,300	Combustion of acetic acid[5].
$[HCO^2CH^3, O^4]$	238,700	Combustion of methyl formate[6].
$[C^2H^5CO^2H, O^7]$	390,600	Combustion of ethyl formate[6].
$[CH^3CO^2CH^3, O^7]$	395,300	Combustion of methyl acetate[6].
$[CH^3CO^2C^2H^5, O^{10}]$	553,700	Combustion of ethyl acetate[5].
$[C^3H^7CO^2H, O^{10}]$	496,940	Combustion of butyric acid[5].
$[C^3H^7CO^2C^2H^5, O^{16}]$	822,500	Combustion of ethyl butyrate[5].
$[C^4H^9CO^2CH^3, O^{16}]$	855,600	Combustion of methyl valerate[5].
$[C^4H^9CO^2C^2H^5, O^{19}]$	1,018,500	Combustion of ethyl valerate[5].
$[CH^3CO^2C^5H^{11}, O^{19}]$	1,036,200	Combustion of amyl acetate[5].
$[CH^3CHO, O^5]$	275,000	Combustion of ethaldehyde[3].
$[C^2H^4O, O^5]$	307,500	Combustion of ethylene oxide[7].

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[1] Longuinine, *Compt. rend.* **90**. 1279: **91**. 297: **92**. 455; 526.

[2] Longuinine, *Comp. rend.* **98**. 94.

[3] Berthelot and Ogier, *Compt. rend.* **92**. 774.

[4] Longuinine, *Comp. rend.* **100**. 63.

[5] Favre and Silbermann, *Ann. Chim. Phys.* (3) **34**. 433.

[6] Ogier, *Compt. rend.* **92**. 671.

[7] Berthelot, *Bull. Soc. Chim.* (2). **39**. 484.

APPENDIX III.

HEATS OF NEUTRALISATION OF ACIDS AND BASES.

I. *Heats of neutralisation of acids according to the determinations of Thomsen*[1].

In the following solutions there are usually 200 formula-weights of water to each formula-weight of sodium hydroxide, or equivalent quantity of acid. Consequently the resulting salt is dissolved in 400 formula-weights of water. The temperature is, as a general rule, between 18° and 20° C.

Table (1) shews the heats of neutralisation of the acids (calculated for one formula-weight) with formation of the normal sodium salts. Table (2) shews the development of heat for different proportions between acid and base, in so far as the normal heat of neutralisation is changed by an excess of acid or base.

(1) HEATS OF NEUTRALISATION; WITH PRODUCTION OF NORMAL SODIUM SALTS.

Monobasic acids.

Name of the acid	Q	[NaOHAq, QAq]
a. Inorganic acids		
1. Hydrofluoric acid	HF	16,270
2. Hydrochloric acid	HCl	13,740
3. Hydrobromic acid	HBr	13,750
4. Hydriodic acid	HI	13,680
5. Sulphydric acid	HSH	7,740
6. Hypochlorous acid	$HClO$	9,980
7. Chloric acid	$HClO_3$	13,760
8. Bromic acid	$HBrO_3$	13,780
9. Iodic acid	HIO_3	13,810
10. Nitric acid	HNO_3	13,680
11. Metaphosphoric acid	HPO_3	14,380
12. Hypophosphorous acid	HPH_2O_2	15,160
13. Perchloric acid	$HClO_4$	14,080

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[1] *Thermochemische Untersuchungen*, 1. 293—299.

b. Organic acids		
14. Hydrocyanic acid	HCN	2,770
15. Formic acid	$HCHO_2$	13,450
16. Acetic acid	$HC_2H_3O_2$	13,400
17. Propionic acid	$HC_3H_5O_2$	13,480
18. Ethyl sulphuric acid	$HC_2H_5SO_4$	13,460
19. Monochloracetic acid	$HC_2H_2ClO_2$	14,280
20. Dichloracetic acid	$HC_2HCl_2O_2$	14,830
21. Trichloracetic acid	$HC_2Cl_3O_2$	13,920

Dibasic acids.

Name of the acid	Q	[2NaOHAq, QAq]
a. Inorganic acids		
22. Fluosilicic acid	H_2SiF_6	26,620
23. Chloroplatinic acid	H_2PtCl_6	27,220
24. Sulphuric acid	H_2SO_4	31,380
25. Selenic acid	H_2SeO_4	30,390
26. Chromic acid	H_2CrO_4	24,720
27. Sulphurous acid	H_2SO_3	28,970
28. Selenious acid	H_2SeO_3	27,020
29. Dithionic acid	$H_2S_2O_6$	27,070
30. Periodic acid	$H_2IH_3O_6$	26,590
31. Arsenious acid	$H_2As_2O_4$	13,780
32. Phosphorous acid	H_2PHO_3	28,450
33. Carbonic acid	H_2CO_3	20,180
34. Boric acid	$H_2B_2O_4$	20,010
35. Silicic acid	H_2SiO_3	5,230
36. Stannic acid	H_2SnO_3	9,570
b. Organic acids		
37. Oxalic acid	$H_2C_2O_4$	28,280
38. Succinic acid	$H_2C_4H_4O_4$	24,160
39. Malic acid	$H_2C_4H_4O_5$	26,170
40. Tartaric acid	$H_2C_4H_4O_6$	25,310

Tribasic acids.

Name of the acid	Q	[3NaOHAq, QAq].
a. Inorganic acids		
41. Phosphoric acid	H_3PO_4	34,030
42. Arsenic acid	H_3AsO_4	35,920
b. Organic acids		
43. Aconitic acid	$H_3C_6H_3O_6$	39,110
44. Citric acid	$H_3C_6H_5O_7$	38,980

Tetrabasic acids.

Name of the acid	Q	[4NaOHAq, QAq]
45. Pyrophosphoric acid	$H_4P_2O_7$	52,740

(2) DEVELOPMENT OF HEAT ON THE FORMATION OF ACID AND BASIC SALTS.

Q	*n*	[*n*NaOHAq, QAq]	*m*	[NaOHAq, *m*QAq]
a. *Monobasic acids*				
HF	1	16,272	1	16,272 Difference 288 = 1·7 per cent. of total heat of neutralisation.
	2	——	2	15,984
HSH	1	7,738 Difference 64	1	7,738
	2	7,802		——
HIO_3	1	13,808 Difference 608	1	13,808 Difference 192 = 1·4 per cent. of total heat of neutralisation.
	2	14,416	2	14,000
HPH_2O_2	$\frac{1}{2}$	7,695	$\frac{1}{2}$	7,637
	1	15,160 Difference 115	1	15,160 Difference 230 = 1·5 per cent. of total heat of neutralisation.
	2	15,275	2	15,390
HPO_3	$\frac{1}{2}$	7,104	$\frac{1}{3}$	5,500
	1	14,376	$\frac{1}{2}$	8,192
	2	16,384	1	14,376 Difference 168 = 1·1 per cent. of total heat of neutralisation.
	3	16,500	2	14,208
b. *Dibasic acids*				
H_2SO_4	$\frac{1}{2}$	7,193	$\frac{1}{4}$	7,842
	1	14,754	$\frac{1}{2}$	15,689
	$\frac{4}{3}$	20,077	$\frac{3}{4}$	15,058
	2	31,378	1	14,754
	4	31,368	2	14,386
H_2SeO_4	1	14,764	$\frac{1}{2}$	15,196
	2	30,392	1	14,764
H_2CrO_4	1	13,134	$\frac{1}{4}$	6,291
	2	24,720	$\frac{1}{2}$	12,360
	4	25,164	1	13,134
H_2SO_3	1	15,870	$\frac{1}{4}$	7,332
	2	28,968	$\frac{1}{2}$	14,484
	4	29,328	1	15,870
H_2SeO_3	1	14,772	$\frac{1}{4}$	6,872
	2	27,024	$\frac{1}{2}$	13,512
	4	27,484	1	14,772

$H_2IH_3O_6$	1	5,150	$\frac{1}{5}$	6,410	
	$\frac{3}{2}$	16,520	$\frac{1}{3}$	9,910	
	2	26,590	$\frac{2}{5}$	11,290	
	$\frac{5}{2}$	28,230	$\frac{1}{2}$	13,300	
	3	29,740	$\frac{2}{3}$	11,010	
	5	32,040	1	5,150	
$H_2As_2O_4$	1	7,300	$\frac{1}{4}$	3,895	
	2	13,780	$\frac{1}{3}$	5,023	
	3	15,070	$\frac{1}{2}$	6,890	
	4	15,580	1	7,300	
H_2PHO_3	$\frac{1}{2}$	7,428	$\frac{1}{3}$	9,647	
	1	14,832	$\frac{1}{2}$	14,244	
	2	28,448	1	14,832	
	3	28,940	2	14,856	
H_2CO_3	1	11,016	$\frac{1}{4}$	5,148	
	2	20,184	$\frac{1}{2}$	10,092	
	4	20,592	1	11,016	
$H_2B_2O_4$	$\frac{1}{3}$	4,524	$\frac{1}{6}$	3,440	
	$\frac{1}{2}$	6,434	$\frac{1}{3}$	6,820	
	1	11,101	$\frac{1}{2}$	10,005	
	$\frac{6}{5}$	12,835	$\frac{2}{3}$	10,307	
	$\frac{3}{2}$	15,460	$\frac{5}{6}$	10,696	
	2	20,010	1	11,101	
	3	20,460	2	12,869	
	6	20,640	3	13,573	
H_2SiO_3	$\frac{1}{3}$	2,652	$\frac{1}{4}$	1,353	
	$\frac{1}{2}$	3,241	$\frac{1}{2}$	2,615	
	$\frac{2}{3}$	3,555	$\frac{3}{4}$	3,548	
	1	4,316	1	4,316	
	$\frac{4}{3}$	4,731	$\frac{3}{2}$	5,332	
	2	5,230	2	6,483	
	4	5,412	3	7,956	
$H_2C_2O_4$	$\frac{1}{2}$	6,904	$\frac{1}{4}$	7,125	
	1	13,844	$\frac{1}{2}$	14,139	
	2	28,278	1	13,844	Difference 36
	4	28,500	2	13,808	
$H_2C_4H_4O_4$	1	12,400	$\frac{1}{4}$	6,096	
	2	24,156	$\frac{1}{2}$	12,078	
	4	24,384	1	12,400	
$H_2C_4H_4O_5$	1	13,035	$\frac{1}{4}$	6,688	
	2	26,168	$\frac{1}{2}$	13,084	Difference 49
	4	26,752	1	13,035	
$H_2C_4H_4O_6$	1	12,442	$\frac{1}{3}$	8,615	
	2	25,314	$\frac{1}{2}$	12,657	Difference 215
	3	25,845	1	12,442	

c. Tribasic and tetrabasic acids.				
H_3PO_4	$\frac{1}{2}$	7,329	$\frac{1}{6}$	5,880
	1	14,829	$\frac{1}{3}$	11,343
	2	27,078	$\frac{1}{2}$	13,539
	3	34,029	1	14,829
	6	35,280	2	14,658
H_3AsO_4	$\frac{1}{2}$	7,362	$\frac{1}{6}$	6,233
	1	14,994	$\frac{1}{3}$	11,972
	2	27,580	$\frac{1}{2}$	13,790
	3	35,916	1	14,994
	6	37,400	2	14,724
$H_3C_6H_3O_6$	1	12,848	$\frac{1}{6}$	6,683
	2	25,781	$\frac{1}{3}$	13,038
	3	39,114	$\frac{1}{2}$	12,890
	6	40,100	1	12,848
$H_3C_6H_5O_7$	1	12,672	$\frac{1}{6}$	6,954
	2	25,445	$\frac{1}{3}$	12,994
	3	38,982	$\frac{1}{2}$	12,722
	6	41,725	1	12,672
$H_4P_2O_7$	1	14,376	$\frac{1}{6}$	9,080
	2	28,644	$\frac{1}{4}$	13,184
	4	52,738	$\frac{1}{2}$	14,322
	6	54,480	1	14,376

II. *Heats of neutralisation of bases according to the determinations of Thomsen*[1].

(1) Direct results of experiments.

NEUTRALISATION OF INORGANIC BASES.

B	[BAq, H^2SO^4Aq]	[BAq, 2HClAq]	[BAq, 2HNO^3Aq]
2LiOH	31,288	27,696	—
2NaOH	31,378	27,488	27,364
2KOH	31,288	27,504	27,544
2TlOH	31,095	47,528	27,380
BaO^2H^2	36,896	27,784	28,264
SrO^2H^2	30,710	27,630	—
CaO^2H^2	31,140	27,900	—
$2NH^3$	28,152	24,544	24,644

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[1] *Thermochemische Untersuchungen,* 1. 412—421.

To these experiments we may add the following, in which a base insoluble in water is dissolved and neutralised by the acids :—

$[CuO, 2H^2SO^4Aq] = 18,130.$

$[PbO, 2HNO^3Aq] = 17,775.$

$[PbO, 2C^2H^4O^2Aq] = 15,468.$

NEUTRALISATION OF ORGANIC BASES.

B	$[BAq, H^2SO^4Aq]$	$[BAq, 2HClAq]$
$2C^2H^5.NH^2$	—	26,880
$2CH^3.NH^2$	—	26,230
$2(CH^3)^2.NH$	—	23,620
$2(CH^3)^3.N$	21,080	17,480
$2(CH^3)^4N.OH$	31,032	27,490
$2(C^2H^5)^3S.OH$	30,590	27,440
$2(NH^3)^4Pt.O^2H^2$	30,850	27,300
$2NH^3O$	—	18,520
$2C^{21}H^{27}N^2O^2.OH$	—	21,680
$2Sb(C^2H^5)^3O$	3,650	—

SIMPLE DECOMPOSITIONS.

a. Sulphuric acid, and salts of barium and lead.

Q	$[QAq, H^2SO^4Aq]$
$BaCl^2$	9,152
BaN^2O^6	8,560
BaS^2O^6	9,136
$BaCl^2O^6$	8,840
$Ba(PO^2H^2)^2$	5,965
$Ba(C^2H^5.SO^4)^2$	9,336
$Ba(C^2H^3O^2)^2$	9,992
PbN^2O^6	5,448
$Pb(C^2H^3O^2)^2$	7,656

b. *Sulphates, and baryta or potash.*

Q	[QAq, BaO^2H^2Aq]	[QAq, 2KOHAq]
Na^2SO^4	5,492	—
K^2SO^4	5,632	—
Tl^2SO^4	5,728	—
$N^2H^8SO^4$	8,792	—
$MgSO^4$	5,840	− 88
$MnSO^4$	10,304	+ 4,912
$NiSO^4$	10,628	5,532
$CoSO^4$	12,224	5,888
$FeSO^4$	12,004	6,340
$CdSO^4$	13,072	7,066
$ZnSO^4$	13,428	7,936
$CuSO^4$	18,456	12,376
$BeSO^4$	—	15,192
Ag^2SO^4	—	16,800
$\frac{1}{3}Fe^2(SO^4)^3$	—	19,984
$\frac{1}{3}La^2(SO^4)^3$	9,458	—
$\frac{1}{3}Ce^2(SO^4)^3$	10,872	—
$\frac{1}{3}Di^2(SO^4)^3$	11,175	—
$\frac{1}{3}Y^2(SO^4)^3$	11,826	—
$\frac{1}{3}Al^2K^2(SO^4)^4$	16,000	10,176
$\frac{1}{3}Cr^2K^2(SO^4)^4$	—	14,848
$\frac{1}{3}Fe^2K^2(SO^4)^4$	—	20,040
$(NH^3O)^2H^2SO^4$	15,320	—
$(NC^6H^7)^2H^2SO^4$	—	12,900

To this group we may add the following reactions:—

$[CuC^4H^6O^4Aq, BaO^2H^2Aq] = 14{,}072$
$[Er^2.6C^2H^3O^2Aq, 3BaO^2H^2Aq] = 25{,}680$
$[2AgNO^3Aq, BaO^2H^2Aq] = 17{,}380$
$[CO^2.N^2H^6Aq, BaO^2H^2Aq] = 4{,}971.$

c. *Partial decompositions.*

n	[$BeSO^4Aq$, *n*KOHAq]	[Fe^2Cl^6Aq, *n*NaOHAq]
$\frac{2}{3}$	6,300	17,040
1	8,930	25,308
$\frac{4}{3}$	11,140	33,408
2	15,190	49,008

n	$[PbN^2O^6Aq, nNaOHAq]$	$[PbC^4H^6O^4Aq, nKOHAq]$
$\frac{1}{2}$	6,396	4,332
1	12,678	8,196
2	11,952	—
4	11,064	—
12	8,260	—

$[PbO.PbC^4H^6O^4Aq,\ 2NO^3HAq] = 12{,}037$
$[K^2SO^4Aq,\ 2NO^3HAq] = -2{,}968$
$[2KNO^3Aq,\ SO^4H^2Aq] = 709.$

Double decompositions.

a. Sulphates, and salts of barium.

Q	$[QAq, BaCl^2Aq]$	$[QAq, BaN^2O^6Aq]$
Na^2SO^4	5,240	4,680
K^2SO^4	5,280	(5,648)
Am^2SO^4	5,408	5,048
$MgSO^4$	5,600	4,936
$MnSO^4$	5,600	—
$CoSO^4$	5,688	—
$CdSO^4$	5,683	5,128
$ZnSO^4$	5,504	—
$CuSO^4$	5,616	5,080
$BeSO^4$	6,660	—

Q	$[QAq, 3BaCl^2Aq]$
$Fe^2 3SO^4$	27,432
$La^2 3SO^4$	20,016
$Ce^2 3SO^4$	21,762
$Di^2 3SO^4$	22,140
$Y^2 3SO^4$	22,842

Q	$[QAq, 4BaCl^2Aq]$
$K^2SO^4.Al^2(SO^4)^3$	25,628
$K^2SO^4.Cr^2(SO^4)^3$	24,544

Q	[QAq, $BaC^4H^6O^4Aq$]	[QAq, $BaC^4H^{10}.S^2O^6Aq$]
Na^2SO^4	5,040	4,884
K^2SO^4	5,136	—
$CaSO^4$	—	5,784
$ZnSO^4$	4,608	—
$CuSO^4$	4,368	5,736
$Fe\frac{2}{3}SO^4$	6,736	—

[Na^2SO^4Aq, $BaCl^2O^6Aq$] = 4,980
[$CuSO^4Aq$, $BaCl^2O^6Aq$] = 5,950
[$Fe^2S^3O^{12}Aq$, $3BaCl^2O^6Aq$] = 28,020
[$Fe^2S^3O^{12}Aq$, $3BaN^2O^6Aq$] = 25,776
[$MgSO^4Aq$, BaS^2O^6Aq] = 5,456
[$CdSO^4Aq$, BaS^2O^6Aq] = 5,600.

b. Salts of lead, strontium, and calcium.

[PbN^2O^6Aq, Na^2SO^4Aq] = 1,712
[$SrCl^2Aq$, Na^2SO^4Aq] = 300
[$CaCl^2Aq$, Na^2SO^4Aq] = 438.

(2) Heats of neutralisation of bases with various acids.

SULPHURIC ACID, HYDROCHLORIC ACID, AND NITRIC ACID.

Inorganic bases.

Q	Sulphuric acid [Q, SO^4H^2Aq]	Hydrochloric acid [Q, 2ClHAq]	Nitric acid [Q, $2NO^3HAq$]
2KOHAq	31,290	27,500	27,540
2NaOHAq	31,380	27,490	27,360
2LiOHAq	31,290	27,700	—
2TlOHAq	31,130	27,520	27,380
BaO^2H^2Aq	36,900*	27,780	28,260
SrO^2H^2Aq	30,710	27,630	—
CaO^2H^2Aq	31,140	27,900	—
MgO^2H^2	31,220	27,690	27,520
MnO^2H^2	26,480	22,950	—
NiO^2H^2	26,110	22,580	—
CoO^2H^2	24,670	21,140	—
FeO^2H^2	24,920	21,390	—
CdO^2H^2	23,820	20,290	20,320
ZnO^2H^2	23,410	19,880	19,830

CuO^2H^2	18,440	14,910	14,890
CuO	18,800	15,270	15,250
PbO	23,380*	15,390	17,770
HgO	—	18,920	6,210
Hg^2O	—	30,070*	5,790
Ag^2O	14,490	42,380*	10,880
N^2H^6	28,150	24,540	24,640
$BeOxH^2O$	16,100	13,640	—

* The numbers marked thus represent the thermal values of the neutralisations when the compounds produced are completely precipitated. In all other cases the compound formed is dissolved in the resulting liquid. For thallous chloride the thermal value is 47,680 if the compound is supposed to remain undissolved.

Q	Sulphuric acid [Q, $3SO^4H^2Aq$]	Hydrochloric acid [Q, $6ClHAq$]
$La^2O^3xH^2O$	3.27,470	3.25,020
$Ce^2O^3xH^2O$	3.26,030	3.24,160
$Di^2O^3xH^2O$	3.25,720	3.23,980
$Y^2O^3xH^2O$	3.25,070	3.23,570
$Al^2O^3xH^2O$	3.20,990	3.18,640
$Cr^2O^3xH^2O$	3.16,440	3.13,730
$Fe^2O^3xH^2O$	3.11,280	3.11,150

Organic bases.

Q	Sulphuric acid [QAq, SO^4H^2Aq]	Hydrochloric acid [QAq, $2ClHAq$]
$Pt(NH^3)_4(OH)_2$	30,850	27,300
$2S(C^2H^5)_3OH$	30,590	27,440
$2N(CH^3)_4OH$	31,030	27,490
$2NH^3$	28,150	24,540
$2NH^2(CH^3)$	—	26,230
$2NH(CH^3)_2$	—	23,620
$2N(CH^3)_3$	21,080	17,480
$2NH^2(C^2H^5)$	—	26,880
$2NH^2(OH)$	21,580	18,520
$2C^{21}H^{27}N^2O^2(OH)$	—	21,680
$Sb(C^2H^5)_3O$	3,650	—
$2NH^2(C^6H^5)$	18,480	(15,480)
$2NH^2(C^7H^7)$	(18,540)	15,240

CARBON DIOXIDE, SULPHYDRIC ACID, AND ACETIC ACID.

Q	Carbon dioxide [Q, CO^2Aq]	Sulphydric acid [Q, $2SH^2Aq$]	Acetic acid [Q, $2C^2H^4O^2Aq$]
$2NaOHAq$	20,180	15,480	26,790
$2KOHAq$	—	—	26,430
BaO^2H^2	21,820	15,750	26,900
SrO^2H^2	20,550	—	—
CaO^2H^2	18,510	—	—
MgO^2H^2	—	15,680	26,400
$2NH^3Aq$	16,850[1]	12,390	24,020
		[Q, SH^2Aq]	
MnO^2H^2	13,230	10,700	—
NiO^2H^2	—	18,630	—
CoO^2H^2	—	17,410	—
FeO^2H^2	—	14,570	—
CdO^2H^2	12,990	27,370	—
ZnO^2H^2	—	17,970	18,030
CuO^2H^2	—	—	12,820
CuO	—	31,670	13,180
PbO	16,700	29,200	15,470
HgO	—	45,300	—
Tl^2O	—	38,490	—
Cu^2O	—	38,530	—
Ag^2O	14,180	58,510	—
$Fe^2O^3\,3H^2O$	—	—	38,020

DITHIONIC ACID, ETHYL-SULPHURIC ACID, AND CHLORIC ACID.

[Q, RAq]

Q	R		
	$S^2O^6H^2$	$2[C^2H^5.SO^4H]$	$2ClO^3H$
$2NaOHAq$	27,070	26,930	27,520
BaO^2H^2Aq	27,760	27,560	28,050
MgO^2H^2	27,540	—	—
CoO^2H^2	—	21,120	—
CdO^2H^2	20,360	—	—
CuO^2H^2	—	14,840	15,550
$\frac{1}{3}Fe^2O^6H^6$	—	—	10,780

---

[1] This number represents the value of the reaction when 100 H_2O is present. *For a solution* with 400 H_2O the value is 15,900 units.

HYPOPHOSPHOROUS ACID AND ARSENIOUS OXIDE.

$[Q, RAq]$

Q	$R = 2PO^2H^3$	$R = As^2O^3$
$2NaOHAq$	30,320	13,780
BaO^2H^2Aq	30,930	14,020

III. *Heats of neutralisation of acids and bases according to the observations of various chemists.*

CARBON ACIDS.

Reaction	Thermal value	Remarks
$[\frac{1}{2}H^4Fe(CN)^6Aq, K^2O^2H^2Aq]$	27,000	
$[\frac{1}{2}H^4Fe(CN)^6Aq, \frac{1}{4}Fe^2O^3]$	12,600	Precipitated ferric oxide used.
$[C^3H^7CO^2HAq, KOHAq]$	14,300	Neutralisation of butyric acid[1].
$[(C^3H^7)^\beta CO^2HAq, KOHAq]$	14,300	Neutralisation of isobutyric acid[1].
$[C^4H^9CO^2HAq, KOHAq]$	14,400	Neutralisation of valeric acid[1].
$[CH^2NH^2CO^2H\ 21H^2O, Na^2O^2H^2\ 21H^2O]$	2,990	Neutralisation of glycocoll by soda[2].
$[CH^2NH^2CO^2H\ 21H^2O, HCl\ 21H^2O]$	980	Neutralisation of glycocoll by acid[2].
$[CH^3CHNH^2CO^2H\ 81H^2O, Na^2O^2H^2\ 21H^2O]$	2,470	Neutralisation of alanine by soda[2].
$[CH^3CHNH^2CO^2H\ 81H^2O, HClH^2O]$	900	Neutralisation of alanine by acid[2].
$[C^2H^4OHCO^2HAq, NaOHAq]$	13,500	Neutralisation of lactic acid[3].

[1] Longuinine, *Compt. rend.* **80.** 568.

[2] Id. *loc. cit.* **86.** 1329.

[3] Berthelot.

PHENOL[1].

$[C^6H^6OAq, QAq]$.

Q	Thermal value	Q	Thermal value
NaOH	7,340	$\frac{2}{5}NH^3$	1,270
$\frac{3}{4}Na^2O^2H^2$	7,460	$\frac{4}{5}NH^3$	1,800
KOH	7,510	$\frac{6}{5}NH^3$	2,180
$\frac{1}{2}CaO^2H^2$	7,420	$\frac{8}{5}NH^3$	2,520
$\frac{1}{6}BaO^2H^2$	2,500	$2NH^3$	2,700
$\frac{1}{3}BaO^2H^2$	5,030		
$\frac{1}{2}BaO^2H^2$	7,480		

GLYCOLLIC ACID[2].

Q	$[2C^2H^4O^3Aq, QAq]$	Q	$[2C^2H^4O^3Aq, Q]$
$K^2O^2H^2$	27,480	PbO	15,100
$Na^2O^2H^2$	27,200	MgO	27,420
$2NH^4OH$	24,460	CuO	15,220
BaO^2H^2	27,800	ZnO	20,800
SrO^2H^2	28,000		
CaO^2H^2	27,800		

ISOMERIC OXYBENZOIC ACIDS[3].

$[C^6H^4OHCO^2HAq, nNaOHAq]$

	ortho-acid	meta-acid	para-acid
$n=1$	12,910	12,800	12,730
$n=2$	810	8,200	8,770
$n=3$	—	700	700

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[1] Berthelot, *Compt. rend.* 73. 672.

[2] De Forcrand, *Compt. rend.* 96. 582. A few more heats of neutralisation are to be found in Naumann's *Thermochemie*, pp. 360—367.

[3] Berthelot and Werner, *Compt. rend.* 100. 1568

APPENDIX IV.

DATA RELATING TO DISSOCIATION-PHENOMENA.

I. *Relative densities of bodies which undergo dissociation.*

Nitrogen tetroxide.

Density (air = 1) calculated for $N_2O_4 = 3{\cdot}18$; for $NO_2 = 1{\cdot}59$.

I. *Pressure* = 760 mm.[1]

Temp.	Density	Temp.	Density	Temp.	Density
26°·7	2·65	49°·7	2·34	90°	1·72
27·6	2·70	52	2·26	100	1·71
28	2·70	55	2·20	100·1	1·68
28·7	2·80	60·2	2·08	100·25	1·72
32	2·65	66	2·03	111·3	1·65
34·6	2·62	68	1·99	121·5	1·62
35·2	2·66	70	1·93	121·8	1·64
35·4	2·53	77·4	1·85	135	1·60
39·8	2·46	79	1·84	151·8	1·50
45·1	2·40	80·6	1·80	154	1·58
49·6	2·27	84·4	1·83	183·2	1·57

II. *Pressure varying*[2].

Temp.	Pressure mm.	Density	Temp.	Pressure mm.	Density	Temp.	Pressure mm.	Density
−6°	125·5	3·01	10°·5	163	2·73	18°	279	2·71
−5	123	2·98	11	190	2·76	18·5	136	2·45
−3	84	2·92	14·5	175	2·62	20	301	2·70
−1	153	2·87	16	228·5	2·65	20·8	153·5	2·46
+1	138	2·84	16·5	224	2·57	21·5	161	2·38
2·5	145	2·84	16·8	172	2·55	22·5	101	2·28
4	172·5	2·85	17·5	172	2·52	22·5	136·5	2·35

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[1] Deville and Troost, *Compt. rend.* **64.** 237.

[2] Naumann, *Ber.* **11.** 2045. See also *ante*, pp. 121 and 126.

PHOSPHORUS PENTACHLORIDE.

Density (air = 1) calculated for $PCl_5 = 7{\cdot}2$; for $PCl_3 + Cl_2 = 3{\cdot}6$.

I. *Pressure* = 760 mm.[1]

Temp.	Density	Ratio of dissociated PCl_5 to possible PCl_5	Temp.	Density	Ratio of dissociated PCl_5 to possible PCl_5
182°	5·08	0·42	274°	3·84	0·98
190	4·99	0·45	288	3·67	0·97
200	4·85	0·49	289	3·69	0·96
230	4·30	0·68	300	3·65	0·98
250	3·99	0·80	327	3 65	0·98
			336	3·66	0·98

II. *Pressure varying*[2].

Temp.	Pressure mm.	Density	Ratio of dissociated PCl_5 to possible PCl_5	Temp.	Pressure mm.	Density	Ratio of dissociated PCl_5 to possible PCl_5
129°	165	6·31	0·14	145°	307	6·33	0·14
129	170	6·63	0·09	145	311	6·70	0·08
129	191	6·18	0·17	145	391	6·55	0·10
137	148	6·47	0·12	148·6	244	5·96	0·21
137	234	6·42	0·13	150·1	225	5·89	0·23
137	243	6·46	0·12	154·7	221	5·62	0·29
137	269	6·54	0·10	167·6	221·8	5·42	0·33
137	281	6·48	0·11	175·8	253·7	5·24	0·30
144·7	247	6·14	0·18	178·5	227·2	5·15	0·40

PHOSPHORUS PENTACHLORIDE AND TRICHLORIDE.

Experiments on the mixed vapours obtained by vaporising PCl_5 into an atmosphere of PCl_3.[3]

p = pressure of the mixture of PCl_5, PCl_3, and Cl_2: π = pressure due to *possible pentachloride* (found by subtracting pressure due to excess of trichloride, as calculated from the theoretical density of PCl_3, from the total pressure): d = density of *possible pentachloride*, calculated from its pressure, π, temperature and volume being known.

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[1] Cahours, *Compt. rend.* **21.** 625: and *Ann. Chim. Phys.* (3) **20.** 369.

[2] Wurtz, *Compt. rend.* **76.** 601; also Troost and Hautefeuille, *Compt. rend.* **83.** 977.

[3] Wurtz, *Compt. rend.* **76.** 601. See further regarding the dissociation of PCl_5, Lemoine, *Études sur les Équilibres Chimiques* 68—72.

Temp.	p	π	d
173°·3	756·1 mm.	423	6·68
165·4	748·4	413	6·80
176·3	751	411	6·88
169·4	724·1	394	7·16
175·3	743·3	343	7·03
164·9	758·5	338	7·38
175·8	760	318	7·00
175·3	756·3	271	7·06
160·5	753·5	214	7·44
165·4	760	194	7·25
170·3	751·2	174	8·30
174·3	742·7	168	7·74

AMYLIC BROMIDE, AND AMYLIC IODIDE[1].

Density (air = 1) of amylic bromide calculated for $C_5H_{11}Br = 5{\cdot}22$: for $C_5H_{10} + HBr = 2{\cdot}61$.

Density (air = 1) of amylic iodide calculated for $C_5H_{11}I = 6{\cdot}84$: for $C_5H_{10} + HI = 3{\cdot}42$.

Pressure = 760 mm.

I. *Amylic bromide.*

Temp.	Density
152°	5·37
155·8	5·18
160·5	5·32
165	5·14
171·2	5·16
173·1	5·18
183·3	5·15
185·5	5·12
193·2	4·84
195·5	4·66
205·2	4·39
215°	4·12
225	4·18
236·5	3·83
248	3·30
262·5	3·09
272	3·11
295	3·19
305·3	3·19
314	2·98
319·2	2·88
360	2·61

II. *Amylic iodide.*

Temp.	Density
143°	6·05
153·5	5·97
160	5·73
168	5·88
210	4·66
262	4·38

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[1] Wurtz, *Compt. rend.* **60**. 728. *Ann. Chim. Phys.* (4). 3. 131.

The chlorides of sulphur[1].

The quantities of the different compounds present at different temperatures were determined.

I. *Dissociation of* SCl_4 *into* $2SCl_2$.

Temp.	SCl_4	SCl_2	Rise of Temp.	Increase in quantity of SCl_2	Mean increase for 1°
− 22°	100·0	0·0			
− 15	42·0	58·0	7°	58·0	8·3
− 10	27·6	72·4	5	13·2	2·6
− 7	22·0	78·0	3	5·7	1·9
− 2	12·0	88·0	5	10·0	2·0
+0·7	8·9	91·3	2·7	3·1	1·1
6·2	2·4	97·6	5·5	6·4	1·1

II. *Dissociation of* $2SCl_2$ *into* S_2Cl_2.

Temp.	SCl_2	S_2Cl_2	Rise of Temp.	Increase in quantity of S_2Cl_2	Mean increase for 10°
20°	93·4	6·6			
30	87·2	12·8	10°	6·2	6·2
50	75·4	24·6	20	11·8	5·9
65	66·8	33·2	15	8·6	5·7
85	54·1	45·9	20	12·7	6·3
90	26·5	73·5	5	27·6	(55·2?)
100	19·5	80·5	10	7·0	7·0
110	12·4	87·6	10	7·1	7·1
120	5·4	94·6	10	7·0	7·0
130	0·0	100·0	10	5·4	5·4

Selenion tetrachloride[2].

Density (air = 1) calculated for $SeCl_4 = 7·63$: for $Se + Cl_4 = 3·815$.

Pressure = 760 mm.

Temp.	Density	Temp.	Density
180°	7·62	245°	5·50
200	7·72	295	5·03
210	6·37	350	4·59
225	5·82		

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[1] Michaelis and Schifferdecker, *Ber.* **6.** 993.

[2] Evans and Ramsay, *C. S. Journal.* **Trans.** for **1884.** 62.

SULPHURIC ACID[1].

Density (air = 1) calculated for $H_2SO_4 = 3{\cdot}386$: for $SO_3 + H_2O = 1{\cdot}693$.

Pressure = 760 mm.

Temp.	Density
332°	2·50
345	2·24
365	2·12
416	1·69
498	1·68

IODINE VAPOUR[2].

Density (air = 1) calculated for $I_2 = 8{\cdot}76$: for $I + I = 4{\cdot}38$.

I. *Pressure* = 760 mm.

Temp.	Density	Temp.	Density
448°	8·74	1040°	7·01
680	8·23	1270	5·82
764	8·28	1400	5·27
855	8·07	1470	5·06
940	7·65		

II. *Pressure varying*[3].

Pressure mm.	Temp.	Density
76	1350°	4·4
152	1400	4·4
228	1500	4·6
304	1450	4·9

For the interval 350°—700° the density was constant and equal to 8·8 even when the pressure was much diminished.

CHLORAL HYDRATE[4]. (B. P. = 95°.)

Density (air = 1) calculated for $C_2Cl_3H_3O_2 = 5{\cdot}72$:

for $C_2Cl_3HO + H_2O = 2{\cdot}86$.

Temp.	Pressure mm.	Density
100	450·5	2·81
78·5	162	2·83

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[1] Wanklyn and Robinson, *Compt. rend.* **56.** 547.

[2] Meier and Crafts, *Ber.* **13.** 851.

[3] Id. *Compt. rend.* **92.** 39.

[4] Naumann, *Ber.* **9.** 822.

CHLORAL ALCOHOLATE[1]. (B. P. = 116°.)

Density (air = 1) calculated for $C_4H_7Cl_3O = 6{\cdot}7$:

for $C_2Cl_3HO + C_2H_6O = 3{\cdot}35$

Temp.	Pressure mm.	Density
100°	756	3·33

BUTYL CHLORAL HYDRATE[2].

Density (air = 1) calculated for $C_4H_7Cl_3O_2 = 6{\cdot}7$:

for $C_4H_5Cl_3O + H_2O = 3{\cdot}35$.

Boiling begins at 100° and temperature rises until 165°, the B. P. of butylchloral, is reached.

Temp.	Pressure mm.	Density
100°	338	3·55
100°	476	3·50

DENSITIES OF VARIOUS COMPLETELY DISSOCIATED VAPOURS[3].

			Density (air = 1)	
	Temp.	pressure mm.	observed	calculated for
Ammonium chloride NH_4Cl	350° 1040		1·01 1·00	0·93 $NH_3 + HCl$
Ammonium bromide NH_4Br	440 860		1·67 1·71	1·70 $NH_3 + HBr$
Ammonium iodide NH_4I	440 860		2·59 2·78	2·50 $NH_3 + HI$
Ammonium sulphydrate NH_4SH	56·7		0·89	0·88 $NH_3 + H_2S$
Ammonium cyanide NH_4CN	100		0·79	0·76 $NH_3 + HCN$
Ethylamine hydrochloride $NH_2(C_2H_5)HCl$	350		1·44	1·41 $NH_2(C_2H_5) + HCl$
Aniline hydrochloride $NH_2(C_6H_5)HCl$	350		2·19	1·83 $NH_2(C_6H_5) + HCl$
Ammonium carbamate[4] $CO(NH_2)(ONH_4)$	37	144	0·896	0·898 $2NH_3 + CO_2$
	47	403	0·890	
	78	160	0·893	
	78	422	0·892	
	100	169	0·891	
	140	760	0·894	

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[1] Wurtz, *Compt. rend.* **85**. 49.

[2] Engel and Moitessier, *Compt. rend.* **90**. 1075.

[3] Deville and Troost, *Compt. rend.* **56**. 895.

[4] Naumann, *Ber.* **4**. 780.

HYDRIODIC ACID.

Lemoine's experiments were made (1) with hydriodic acid, (2) with a mixture of hydrogen and iodine vapour. He studied both the rate and the limit of dissociation at specified temperatures and pressures; and also the influence of an excess of either constituent on the final equilibrium of the system.

His most important results are given in the following tables.

I. *Rate of dissociation.*

Hydrogen and iodine vapour heated to 350°.						Hydriodic acid heated to 350°.	
Pressure = 3040 mm.		Pressure = 1520 mm.		Pressure = 684 mm.		Pressure = 1520 mm.	
Duration of Experiment in hours	Ratio of free to total hydrogen	Duration of Experiment in hours	Ratio of free to total hydrogen	Duration of Experiment in hours	Ratio of free to total hydrogen	Duration of Experiment in hours	Ratio of free to total hydrogen
8	0·4	3	0·88	8	0·97	9	0·03
8	0·48	8	0·69	34	0·61	70	0·20
23	0·25	34	0·48	75	0·53	167	0·21
33½	0·29 (?)	76	0·29	79½	0·48 (?)	259	0·186
72	0·21	327	0·185	215	0·35		
76	0·22			377	0·22		
117	0·22			407	0·18 (??)		
140	0·22						

When equilibrium is established at a pressure of two atmospheres, the ratio seems to be about 0·186.

II. *Limit of dissociation.*

Hydrogen and iodine vapour heated to 440°.							
Pressure = 3420 mm.		Pressure = 1750 mm.		Pressure = 684 mm.		Pressure = 152 mm.	
Duration of Experiment in hours	Ratio of free to total hydrogen	Duration of Experiment in hours	Ratio of free to total hydrogen	Duration of Experiment in hours	Ratio of free to total hydrogen	Duration of Experiment in hours	Ratio of free to total hydrogen
1·85	0·24	0·33	0·31	24·5	0·27	119	0·297
22	0·24	9·5	0·25	25	0·25	119	0·297
22	0·24	18	0·26				

Lemoine notices some sources of error in these experiments. He concludes that when equilibrium is established at a pressure of 4½ atmospheres the ratio of free to total hydrogen is 0·25, and when established at 0·9 atmospheres the ratio is 0·30.

III. *Influence of excess of one constituent on the final equilibrium of the system.*

Hydrogen and iodine vapour heated to 440°, pressure being = 1750 mm.

Ratio of H : I	Ratio of HI dissociated : HI possible[1]	Ratio of HI produced : HI possible[1]
H : I	0·24	0·76
H : ·784 I	0·17	0·83
H : ·527 I	0·14	0·86
H : ·258 I	0·12	0·88

The results on which the foregoing table is based may also be represented in this way:—

Composition of initial system	Ratio of HI dissociated : HI possible	Ratio of HI produced : HI possible
H + I	0·26	0·74
2H + I	0·16	0·84
3H + I	0·13 (?)	0·87
4H + I	0·12	0·88

COMPOUND FORMED BY THE ACTION OF HYDROCHLORIC ACID ON METHYLIC OXIDE; $C_2H_6O.\ HCl$.

The influence of (1) temperature, (2) pressure, (3) excess of one constituent, on the dissociation of $C_2H_6O.\ HCl$ has been studied by Friedel[2].

I. *Influence of temperature.*

Pressure approximately 760 mm.

Temp.	Density	Ratio of dissociated : total gas[3]	Temp.	Density	Ratio of dissociated : total gas[3]
5°	1·645	0·75	55°	1·498	0·93
15	1·570	0·84	65	1·488	0·94
25	1·537	0·88	75	1·483	0·95
35	1·516	0·90	85	1·474	0·96
45	1·506	0·92	95	1·467	0·97

Theoretical density if decomposition were complete = 1·43; if no decomposition occurred = 2·854.

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[1] That is, possible if all the iodine had combined with hydrogen.

[2] *Bull. Soc. Chim.* (2). **24**. 160; 241.

[3] Calculated by Lemoine. See his *Études sur les Équilibres chimiques*, 87—91.

II. *Influence of pressure.*

Temperature approximately 21°.

Pressure	Density	Ratio of dissociated : total gas[1]	Pressure	Density	Ratio of dissociated : total gas[1]
670 mm.	1·537	0·88	950 mm.	1·583	0·82
750 „	1·548	0·86	1050 „	1·602	0·80
850 „	1·565	0·84	1100 „	1·611	0·79

Theoretical density if decomposition were complete = 1·43; if no decomposition occurred = 2·854.

III. *Influence of excess of one constituent.*

The contraction occurring on mixing varying volumes of $(CH_3)_2O$ and HCl gases was measured. Temp. approximately 20°; pressure approximately 760 mm.

Excess of one constituent, referred to the total volume of the mixture.	Contraction, referred to the total quantity of gas which could combine.	
		Ratio of dissociated : total gas[1]
(1) Excess of $(CH_3)_2O$.		
0	5·8 per cent.	0·884
0·1	7·7 „	0·846
0·2	8·9 „	0·822
0·4	10·8 „	0·784
0·6	11·8 „	0·764
(2) Excess of HCl.		
0	5·8 „	0·884
0·1	7·7 „	0·846
0·2	8·6 „	0·828
0·4	10·4 „	0·792
0·6	11·2 „	0·776

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[1] Calculated by Lemoine. See his *Études sur les Équilibres chimiques*, 87—91.

18—2

II. *Equilibrium-pressures of different dissociating systems at various temperatures.*

AMMONIUM CARBAMATE.

$CO(NH_2)ONH_4$ dissociates into $2NH_3 + CO_2$[1].

Temp.	Equilibrium-pressure	Temp.	Equilibrium-pressure
− 15°	2·6 mm.	26°	97·5 mm.
− 10	4·8 „	28	110 „
− 5	7·5 „	30	124 „
0	12·4 „	32	143 „
+ 2	15·7 „	34	166 „
4	19 „	36	191 „
6	22 „	38	219 „
8	25·7 „	40	248 „
10	29·8 „	42	278 „
12	34 „	44	316 „
14	39 „	46	354 „
16	46·5 „	48	402 „
18	53·7 „	50	470 „
20	62·4 „	55	600 „
22	72 „	60	770 „
24	84·8 „		

DOUBLE COMPOUNDS OF AMMONIA.

The double compounds of silver chloride and ammonia dissociate into their constituents[2], (1) $AgCl . 3NH_3$ into $AgCl + 3NH_3$; (2) $2AgCl . 3NH_3 = 2AgCl + 3NH_3$.

	Equilibrium-pressures (mm.)	
Temp.	$AgCl . 3NH_3$	$2AgCl . 3NH_3$
6°	—	22
7	—	23·4
8	432	24·9
9	446	26·5
10	465	28·2
11	491	30
12	520	31·9
13	551	33·9
14	584	36
15	618	38·3
16	653	40·9
17	688	43·7
18	723	46·6
19	758	49·6
20	793	52·6
21	829	55·6

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[1] Naumann. *Ber.* 4. 781; 815. See also Id. *loc. cit.* 18. 1157.

[2] Horst [illegible] 756.

The double compound of calcium chloride and ammonia, $CaCl_2 8NH_3$, dissociates into its constituents[1] $CaCl_2 + 8NH_3$.

	Temp.	Equilibrium-pressure (mm.)
Temp. rising	0	120·5
	10·8	209·2
	11·6	239
	13	259·6
	15·7	295
	17·8	320
	21·4	380
	30·4	572
	36·8	899
	43·4	1283
Temp. falling	21·5	599
	19·9	436
	16·3	310
	0	169·5

CHLORAL HYDRATE.

$CCl_3 . CHO . H_2O$ dissociates into $CCl_3CHO + H_2O$[2].

Temp.	Equilibrium-pressure	Temp.	Equilibrium-pressure
0°	230 mm.	8°·8	772 mm.
3·3	375 „	9·1	776 „
3·6	400 „	9·5	793 „
5	481 „	10·1	832 „
5·7	530 „	11	950 „
5·9	545 „	11·5	1015 „
6·6	571 „	11·7	1032 „
7·2	595 „	12·9	1245 „
7·6	644 „	14·5	1400 „
8	671 „		

BUTYLCHLORAL HYDRATE.

$C_3H_4Cl_3 . CHO . H_2O$ dissociates into $C_3H_4Cl_3CHO + H_2O$[3].

Temp.	Equilibrium-pressure
16°·8	18·3 mm.
46	62·8 „
65	125 „
78·4	331 „

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[1] Weinhold, *Pogg.* **149.** 220.

[2] Isambert, *Compt. rend.* **86.** 481.

[3] Engel and Moitessier, *Compt. rend.* **90.** 1075.

PHOSPHORUS.

When ordinary phosphorus is heated in a closed vessel it is partially changed into red phosphorus: for each temperature there is a maximum pressure exerted by the phosphorus vapour at which the change stops.

The following numbers are taken from a paper by Troost and Hautefeuille[1];—

Temperature	Equilibrium-pressure in atmospheres
360°	0·1
440	1·75
487	6·8
510	10·8
531	16
550	31
577	56

CHLORINE HYDRATE.

Cl $5H_2O$, formed at a temperature less than 8°, dissociates on heating into chlorine and water[2].

Temp.	Equilibrium-pressure mm.	Temp.	Equilibrium-pressure mm.
0°	230	8°·8	722
3·3	375	9·1	776
3·6	400	9·5	793
5·0	481	10·1	832
5·7	530	11	950
5·9	545	11·5	1015
6·6	571	11·7	1032
7·2	595	12·9	1245
7·6	644	14·5	1400
8·0	671		

HYDRATED SALTS.

Many hydrated salts lose water when heated in a closed vessel. When the pressure of the water-vapour evolved reaches a certain amount, for a specified temperature, the process stops. The following numbers were obtained by G. Wiedemann[1].

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[1] *Ann. Chim. Phys.* (5). **2.** 145.

[2] Isambert, *Compt. rend.* **86.** 481.

$MgSO_47H_2O$		$ZnSO_47H_2O$		$CoSO_47H_2O$	
Temp.	Equilibrium-pressure	Temp.	Equilibrium-pressure	Temp.	Equilibrium-pressure
24°·3	17·8 mm.	11°·6	5·8 mm.	13°·6	9·8 mm.
29·8	26·5 „	16·5	7·3 „	20	13·4 „
35	35·6 „	20·2	10·1 „	22·1	15·9 „
40·2	46·3 „	22	12·6 „	25·1	17·3 „
45·4	60·9 „	30	20·3 „	26·2	19·2 „
51·9	81·9 „	34·5	40·7 „	35	35·6 „
61·2	129·2 „	40	54·9 „	40	47·4 „
61·8	132·5 „	45	71·4 „	45	62·3 „
70·2	188·9 „	50	92·9 „	50	78·5 „
		55	117·5 „	55	106
		60	113·9 „	60	133·4 „
		66	145·5 „	64·9	165·8 „
		70	170·8 „	70	207·2 „
		75	221·2 „	75	252·6 „
		78·8	258·5 „	80	306·4 „
		85·5	376·4 „	85	377·4 „
		88	427 „	90	447·9 „

$NiSO_47H_2O$		$FeSO_47H_2O$	
Temp.	Equilibrium-pressure	Temp.	Equilibrium-pressure
13°·6	11·2 mm.	21°	13·3 mm.
20·2	16·5 „	25·5	16·9 „
25	19·3 „	29·9	21·2 „
30	26·3 „	36·3	30·1 „
35	36·4 „	40·4	41·1 „
40	46·9 „	45	55·1 „
45·2	60·1 „	50	74·8 „
50	81·4 „	56·3	109·1 „
56	108·2 „	59·9	128·7 „
60	130·6 „	65	163·4 „
65	163·8 „	70	205·2 „
70	204·3 „	75	263·9 „
75	249·6 „	80	321·9 „
80·1	306·9 „	85	397·7 „
85·2	368·5 „	90	478·2 „
90	436·8 „	93·5	548·9 „

[1] *Pogg.* Jubelbd. 474.

III. *So-called abnormal vapour densities.*

FORMIC ACID.

Experiments of Bineau[1]. *Temperature and pressure varying.* Density (air = 1) calculated for $CH_2O_2 = 1·59$. B.P. = 101°.

Temp.	Pressure mm.	Density	Temp.	Pressure mm.	Density
10°·5	14·7	3·23	99°·5	684	2·49
11	7·3	3·02	99·5	690	2·52
12·5	15·2	3·14	101	650	2·41
15	7·6	2·93	101	693	2·44
15·5	2·6	2·86	105	630	2·32
16	15·9	3·13	105	650	2·33
18·5	23·5	3·23	105	691	2·35
20	2·8	2·80	108	687	2·31
20	8	2·85	111	608	2·13
20	16·7	2·94	111·5	690	2·25
22	25·2	3·05	111·5	690	2·22
24·5	17·4	2·86	115	655	2·13
29	27·4	2·83	115·5	640	2·16
30	18·3	2·76	115·5	649	2·20
30·5	8·8	2·69	117·5	688	2·13
31·5	3·1	2·60	118	650	2·13
34·5	28·9	2·77	118	655	2·14
99·5	557	2·34	124·5	640	2·04
99·5	602	2·40	124·5	670	2·06
99·5	619	2·41	125·5	645	2·03
99·5	641	2·42	125·5	687	2·05
99·5	662	2·44	184	750	1·68
99·5	676	2·46	216	690	1·61

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[1] *Ann. Chim. Phys.* (3). 18. 240.

ACETIC ACID.

Density (air = 1) calculated for $C_2H_4O_2 = 2{\cdot}08$. B.P. = 119°.

I. *Pressure* = 760 *mm.*[1]

Temp.	Density	Temp.	Density	Temp.	Density
124°	3·20	162°	2·59	250°	2·08
125	3·20	165	2·65	252	2·09
128·6	3·08	170	2·48	254·6	2·14
130	3·11	171	2·42	272	2·09
131·3	3·08	180	2·44	280	2·08
134·3	3·11	181·7	2·47	295	2·08
140	2·90	190	2·35	300	2·08
145	2·75	200	2·24	308	2·08
150	2·75	219	2·15	321	2·08
152	2·72	230	2·09	327	2·08
160	2·48	231	2·11	336	2·08
160·3	2·65	233·5	2·20	338	2·08
		240	2·09		

II. *Pressure varying*[2].

Temp.	Pressure mm.	Density	Temp.	Pressure mm.	Density
11°·5	3·76	3·88	22°	8·64	3·85
12	2·44	3·80	24	5·75	3·70
12	5·23	3·92	28	10·03	3·75
19	2·60	3·66	30	6·03	3·60
19	4·00	3·75	35	11·19	3·64
20	5·56	3·77	36·5	11·32	3·62
20	8·55	3·88	129	633	2·88
20·5	10·03	3·95	[3]130	30·6	2·10[3]
21	4·06	3·72	[3]130	59·7	2·12[3]
22	2·70	3·56	132	757	2·86

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[1] Cahours, *Compt. rend.* **20.** 51. Horstmann, *Annalen.* **Supplbd. 6.** 63.

[2] Bineau, *Annalen.* **60.** 160.

[3] Observation by Troost, *Compt. rend.* **86.** 1395.

ACETIC ACID.

Experiments by Naumann[1]. *Temperature and Pressure varying.*

Temp. 78°		Temp. 100°		Temp. 110°	
Pressure (mm.)	Density	Pressure	Density	Pressure	Density
164	3·41	393·5	3·44	411	3·31
149	3·34	342·3	3·37	359·3	3·22
137	3·26	258	3·17	197	2·91
113	3·25	232	3·12	166·5	2·81
80	3·06	186	3·06	138·5	2·78
66	3·04	168	3·01	98·5	2·61
		156	2·98	84	2·49
		130	2·94		
		92	2·76		
		77·7	2·66		

Temp. 120°		Temp. 130°		Temp. 140°	
Pressure	Density	Pressure	Density	Pressure	Density
432	3·14	455	2·97	477	2·82
377·5	3·06	398·5	2·89	417·5	2·75
252	2·94	274	2·68	287·5	2·54
209	2·75	221	2·61	232	2·50
180	2·61	201	2·56	199	2·40
149	2·60	188	2·50	168·2	2·32
106	2·46	157·5	2·47	117·3	2·27
89·5	2·37	112·5	2·34	98	2·24
		93	2·32		

Temp. 150°		Temp. 160°		Temp. 185°	
Pressure	Density	Pressure	Density	Pressure	Density
498·5	2·68	253	2·31	565	2·36
436·5	2·63	129·2	2·11	495	2·31
300	2·44			382	2·25
243	2·40			335	2·23
208·2	2·29			269	2·22
175	2·26			230	2·14
103	2·16			191·5	2·13
				110·5	2·11

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[1] *Annalen.* **155.** 325.

BUTYRIC ACID.

Experiments of Cahours[1]. *Pressure* = 760 *mm.*

Density (air = 1) calculated for $C_4H_8O_2$ = 3·04. B.P. = 157°.

Temp.	Density	Temp.	Density
177°	3·68	261°	3·07
208	3·44	290	3·07
228	3·22	310	3·07
249	3·10	330	3·07

ETHYLIC OXIDE.

Experiments of Horstmann[2]. *Temperature and Pressure varying.*

Density (air = 1) calculated for $(C_2H_5)_2O$ = 2·56. B.P. = 35°.

Temp.	Pressure (mm.)	Density	Temp.	Pressure	Density
39°·7	763	2·65	93°·1	762·4	2·60
46·1	764·5	2·67	102·8	756·2	2·60
52·2	740·5	2·64	115·3	755·8	2·58
53·7	745	2·65	130·6	756·7	2·58
66·1	754·3	2·65	132·6	742·5	2·57
81·1	762·6	2·61	204·5	757·1	2·57

WATER[2].

Density (air = 1) calculated for H_2O = 0·622.

Temp.	Pressure	Density
108°·8	752·7	0·653
129·1	740·3	0·633
175·4	764·1	0·625
200·2	755·9	0·626

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[1] *Compt. rend.* **20.** 51.

[2] Horstmann, *Annalen.* **Supplbd. 6.** 63.

ETHEREAL SALTS.

Temperature and Pressure varying. Experiments of Schoop[1].

I. *Methyl formate.*

Density (air = 1) calculated for HCO_2CH_3 = 2·0783. B.P. = 31°·5.

Temp. −0°·4		Temp. 34°	
Pressure (mm.)	Density	Pressure	Density
170·4	2·0708	722	2·0980
		440·5	2·0737
		315·5	2·0567
		247·2	2·0458

Temp. 64°·4		Temp. 99°·4	
Pressure	Density	Pressure	Density
801·2	2·0759	887	2·0650
485·5	2·0638	538·3	2·0546
348·9	2·0493	385·8	2·0436
272·1	2·0373	300·4	2·0382

II. *Ethyl formate.*

Density (air = 1) calculated for $HCO_2C_2H_5$ = 2·5632. B.P. = 54°.

Temp. 35°		Temp. 46°·3	
Pressure	Density	Pressure	Density
174·7	2·5613	181·2	2·5599
235·2	2·5839	245·6	2·5694
328	2·5998	340·8	2·5938
		524	2·6207

Temp. 65°·7		Temp. 99°·5	
Pressure	Density	Pressure	Density
887·9	2·6391	1004·4	2·6144
599·3	2·6071	660·3	2·5764
361·4	2·5910	400·5	2·570
260·4	2·5682	287	2·5567
192	2·5588	212	2·5477

[1] ied. Ann. 12. 550.

III. *Methyl acetate.*

Density (air = 1) calculated for $CH_3CO_2CH_3$ = 2·5632. B.P. = 53°·5.

Temp. 34°·8		Temp. 46°·6	
Pressure	Density	Pressure	Density
297·4	2·5885	338·7	2·5882
233·8	2·5729	244·8	2·5591
173·6	2·5543	180·4	2·5495

Temp. 65°·3		Temp. 99°·5	
Pressure	Density	Pressure	Density
593·1	2·5997	980	2·6079
359·8	2·5817	656	2·5810
257·5	2·5596	399·3	2·5612
191·6	2·5467	285	2·5490
		211·3	2·5207

IV. *Propyl formate.*

Density (air = 1) calculated for $HCO_2C_3H_7$ = 3·0481. B.P. = 83°.

Temp. 34°·7. Pressure 121·8 mm. Density 3·2267.

Temp. 65°·3		Temp. 80°·2	
Pressure	Density	Pressure	Density
152·2	2·9820	157·7	2·9812
206·1	2·9902	215·4	2·9859
287·2	3·0144	301	3·0017
403·2	3·0478	494·1	3·0487
		700·1	3·0597

Temp. 99°·4		Temp. 128°	
Pressure	Density	Pressure	Density
1076·1	3·0675	116·8	3·0598
780·4	3·0336	842	3·0262
521·6	3·0219	564·1	3·0048
317·6	2·9948	343·5	2·9829
228·8	2·9665	244·3	2·9726
168·9	2·9596	181·7	2·9700

V. *Ethyl acetate.*

Density (air = 1) calculated for $CH_3CO_2C_2H_5$ = 3·0481. B.P. = 77°.
Temp. 35°. Pressure 128·8 mm. Density 3·0606.

Temp. 65°·1		Temp. 79°·6	
Pressure	Density	Pressure	Density
148·2	3·0521	706·7	3·1776
199·8	3·0752	474·4	3·1365
279·4	3·1008	289·1	3·0993
454·7	3·1438	208·3	3·0800
		154	3·0557

Temp. 99°·4		Temp. 128°	
Pressure	Density	Pressure	Density
1074·3	3·1722	1076·1	3·1335
759·4	3·1226	818·1	3·1196
503·7	3·1136	546·3	3·0892
306·9	3·0825	331	3·0850
220·5	3·0656	237·5	3·0626
163·3	3·0491	174·6	3·0379

VI. *Methyl propionate.*

Density (air = 1) calculated for $C_2H_5CO_2CH_3$ = 3·0481. B.P. = 78°·7.

Temp. 64°·9		Temp. 78°·96	
Pressure	Density	Pressure	Density
113·2	3·0364	118	3·0377
153	3·0523	159·1	3·0466
211·8	3·0859	221	3·0768
348·1	3·1136	365	3·0924
		549·8	3·1090

Temp. 99°·8		Temp. 127°·8	
Pressure	Density	Pressure	Density
776·7	3·1103	817·8	3·0951
579·5	3·1026	624·7	3·0894
387·2	3·0812	417·7	3·0853
234·3	3·0646	251·2	3·0695
168·6	3·0421	180·3	3·0539
124·5	3·0242	132·3	3·0541

BROMINE AND CHLORINE[1].

I. *Bromine.*

Temp. above B.P.	Density	Deviation (in per cents) from normal density	Differences
40°	5·7115	3·381	
60	5·6809	2·827	·554
80	5·6503	2·273	·554
100	5·6197	1·719	·554
120	5·5891	1·165	·554
140	5·5585	0·612	·553
160	5·5279	0·058	·554

II. *Chlorine.*

Temp. above B.P.	Density	Deviation (in per cents) from normal density	Differences
40°	2·4844	1·397	
60	2·4810	1·261	·136
80	2·4776	1·122	·139
100	2·4742	0·984	·138
120	2·4708	0·845	·139
140	2·4674	0·706	·139
160	2·4641	0·571	·135
180	2·4606	0·429	·142
200	2·4572	0·290	·139
220	2·4538	0·102	·188
240	2·4504	0·000	

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[1] Jahns, *Ber.* **15.** 1238.

V. *Ethyl acetate.*

Density (air = 1) calculated for $CH_3CO_2C_2H_5$ = 3·0481. B.P. = 77°.
Temp. 35°. Pressure 128·8 mm. Density 3·0606.

Temp. 65°·1		Temp. 79°·6	
Pressure	Density	Pressure	Density
148·2	3·0521	706·7	3·1776
199·8	3·0752	474·4	3·1365
279·4	3·1008	289·1	3·0993
454·7	3·1438	208·3	3·0800
		154	3·0557

Temp. 99°·4		Temp. 128°	
Pressure	Density	Pressure	Density
1074·3	3·1722	1076·1	3·1335
759·4	3·1226	818·1	3·1196
503·7	3·1136	546·3	3·0892
306·9	3·0825	331	3·0850
220·5	3·0656	237·5	3·0626
163·3	3·0491	174·6	3·0379

VI. *Methyl propionate.*

Density (air = 1) calculated for $C_2H_5CO_2CH_3$ = 3·0481. B.P. = 78°·7.

Temp. 64°·9		Temp. 78°·96	
Pressure	Density	Pressure	Density
113·2	3·0364	118	3·0377
153	3·0523	159·1	3·0466
211·8	3·0859	221	3·0768
348·1	3·1136	365	3·0924
		549·8	3·1090

Temp. 99°·3		Temp. 127°·8	
Pressure	Density	Pressure	Density
776·7	3·1103	817·8	3·0951
579·5	3·1026	624·7	3·0894
387·2	3·0812	417·7	3·0853
234·3	3·0646	251·2	3·0695
168·6	3·0421	180·3	3·0539
124·5	3·0242	132·3	3·0541

Bromine and chlorine[1].

I. *Bromine.*

Temp. above B.P.	Density	Deviation (in per cents) from normal density	Differences
40°	5·7115	3·381	
60	5·6809	2·827	·554
80	5·6503	2·273	·554
100	5·6197	1·719	·554
120	5·5891	1·165	·554
140	5·5585	0·612	·553
160	5·5279	0·058	·554

II. *Chlorine.*

Temp. above B.P.	Density	Deviation (in per cents) from normal density	Differences
40°	2·4844	1·397	
60	2·4810	1·261	·136
80	2·4776	1·122	·139
100	2·4742	0·984	·138
120	2·4708	0·845	·139
140	2·4674	0·706	·139
160	2·4641	0·571	·135
180	2·4606	0·429	·142
200	2·4572	0·290	·139
220	2·4538	0·102	·188
240	2·4504	0·000	

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[1] Jahns, *Ber.* **15**. 1238.

APPENDIX V.

HEATS OF SOLUTION, DILUTION AND HYDRATION.

I. *Values determined by Thomsen*[1].

HEATS OF SOLUTION AND DILUTION OF ACIDS.

$[SO^4H^2, mH^2O]$			$[NO^3H, mH^2O]$		
m	Results of experiment	Calculated according to the formula $\frac{m \times 17{,}860}{m + 1\cdot7983}$	m	Results of experiment	Calculated according to the formula $\frac{m \times 8{,}974}{m + 1\cdot737}$
1	6,379	6,382	0·5	2,005	2,008
2	9,418	9,404	1	3,285	3,285
3	11,137	11,167	1·5	4,160	4,160
4	—	12,320	2	—	4,808
5	13,108	13,135	2·5	5,276	5,301
9	14,952	14,886	3	5,710	5,690
19	16,256	16,315	4	—	6,266
49	16,684	—	5	6,665	6,668
99	16,858	—	10	7,318	—
199	17,065	—	20	7,458	—
399	17,313	—	40	7,436	—
799	17,641	—	80	7,421	—
1,599	17,857	17,840	100	7,439	—
			160	7,450	—
			320	7,493	—

$[SO^3, H^2O] = 21{,}320$

$[2SO^3, H^2O] = 24{,}020$

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[1] *Thermochemische Untersuchungen*, 3. 34—39; 179—180; and 193—204.

m	$[C^2H^4O^2, mH^2O]$	$[CH^2O^2, mH^2O]$	m	$[H^3PO^4, mH^2O]$
0·5	− 130	+ 124	1	1,741
1	− 152	+ 172	3	3,298
1·5	− 165	—	9	4,509
2	− 156	+ 167	20	4,938
4	− 111	—	50	5,169
8	− 2	—	100	5,269
20	+ 173	—	200	5,355
50	+ 278	+ 126		
100	+ 335	+ 148		
200	+ 375	+ 149		

These values all refer to the acids as liquid bodies. They hold good therefore for fused sulphuric acid and orthophosphoric acid. On the other hand, the following values are valid for crystallised tartaric acid :

$m=$	6	20	50	100	200	400
$[C^4H^6O^6, mH^2O]$	− 3,240	− 3,307	− 3,452	− 3,516	− 3,566	− 3,600

HEATS OF SOLUTION OF HYDROCHLORIC, HYDROBROMIC, AND HYDRIODIC ACID, IN VARIOUS QUANTITIES OF WATER.

m	$[HCl, mH^2O]$	$[HBr, mH^2O]$	$[HI, mH^2O]$
2	11,365	(13,860)	(12,540)
3	13,362	15,910	14,810
5	14,959	17,620	17,380
6	—	18,250	—
10	16,157	19,100	18,580
20	16,756	19,470	18,990
50	17,115	19,820	19,140
100	17,235	19,910	19,180
300	17,315	—	—
500	—	19,940	19,210

HEATS OF DILUTION OF SOLUTIONS OF POTASSIUM AND SODIUM HYDROXIDES.

$m+3$	$[KOH.3H^2O, mH^2O]$	$[NaOH.3H^2O, mH^2O]$
5	1,496	2,131
7	2,095	2,889
9	2,364	3,093
20	2,678	3,283
25	—	3,263
50	2,738	3,113
100	2,748	3,000
200	2,751	2,940

For a solution of ammonia, $NH_3+3{\cdot}2H^2O$, the thermal values of dilution, up to 15, 25, and 50 formula-weights of water, amount to 324, 350, and 380 respectively.

HEATS OF DILUTION OF SOLUTIONS OF SALTS.

The numbers in the following tables give the development of heat on dilution of a solution of the salt containing n formula-weights of water by m formula-weights of water, and therefore correspond to the formula

$$[Q.nH^2O, mH^2O],$$

supposing Q to denote the formula-weight, or double the formula-weight, as the case may be, of the dissolved dehydrated salt. L_c denotes the heat of solution of the dehydrated salt for c formula-weights of water.

Nitrates.

$n+m$	$Na_2N_2O_6$ $n=12$	$N_2H_8.N_2O_6$ $n=5$	SrN_2O_6 $n=20$	PbN_2O_6 $n=40$	MgN_2O_6 $n=10$	MnN_2O_6 $n=10$	ZnN_2O_6 $n=10$	CuN_2O_6 $n=10$
6	—	− 668	—	—	—	—	—	—
10	—	− 1,282	—	—	—	0	0	0
12	0	—	—	—	0	—	—	474
15	—	—	—	—	262	934	913	744
20	—	− 2,492	0	—	412	1,294	1,148	940
40	—	− 3,578	—	0	—	—	—	—
50	− 2,262	—	−1,263	—	404	1,528	1,203	904
100	− 3,288	− 4,584	−1,944	−1,227	364	1,541	1,111	776
200	− 3,860	− 5,018	−2,366	−1,984	370	1,573	1,071	729
400	− 4,192	− 5,228	−2,515	−2,501	421	1,648	—	—
L_{400}	*−10,060*	−12,640	−4,620	−7,610	positive	positive	positive	positive

Sulphates.

$n+m$	Na_2SO_4 $n=50$	$N_2H_8SO_4$ $n=10$	$MgSO_4$[1] $n=20$	$MnSO_4$ $n=20$	$ZnSO_4$ $n=20$	$CuSO_4$ $n=60$
20	—	—	0	0	0	—
30	—	- 253	—	—	—	—
50	0	- 437	+ 279	+ 532	+ 318	—
60	—	—	—	—	—	0
100	- 665	- 632	+ 324	+ 714	+ 377	+ 41
200	- 1,132	- 750	+ 393	+ 792	+ 390	+ 116
400	- 1,383	—	—	—	—	—
800	- 1,483	—	—	—	—	—
L_{400}	+ 460	- 2,370	+ 20,280	+ 13,790	+ 18,430	+ 15,800

Bisulphates. *Carbonates.*

$n+m$	$KHSO_4$ $n=20$	$NaHSO_4$ $n=10$	NH_4HSO_4 $n=10$	K_2CO_3 $n=10$	Na_2CO_3 $n=30$	NH_4HCO_3 $n=40$
20	—	+ 436	—	—	—	—
50	- 64	+ 520	+ 486	- 122	- 556	- 176
100	- 30	+ 558	+ 594	- 406	- 1,190	- 288
200	+ 108	+ 702	+ 788	- 598	- 1,601	- 384
400	+ 382	+ 969	+ 1,048	- 749	—	—
800	+ 766	+ 1,189	+ 1,366	—	—	—
L_{200}	- 3,800	+ 1,190	- 20	+ 6,490	+ 5,640	negative

Acetates. *Tartrate.*

$n+m$	$2(KC_2H_3O_2)$ $n=10$	$2(NaC_2H_3O_2)$ $n=20$	$2(NH_4.C_2H_3O_2)$ $n=4$	$Zn(C_2H_3O_2)_2$ $n=50$	$(NH_4)_2C_4H_4O_6$ $n=21$
10	0	—	1,088	—	—
20	1,580	0	1,800	—	—
30	—	—	—	—	- 296
50	2,472	664	2,544	0	- 648
100	2,786	832	2,988	1,189	- 1,014
200	2,998	936	3,250	2,248	- 1,242
400	3,144	—	3,432	3,134	- 1,358
L_{400}	+ 6,680	+ 7,740	positive	positive	negative

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[1] But see Pickering, *C. S. Journal*, **Trans.** for **1886.** 100.

Chlorides.

$n+m$	Na_2Cl_2 $n=20$	$(NH_4)_2Cl_2$ $n=20$	$CaCl_2$ $n=10$	$MgCl_2$ $n=10$	$ZnCl_2$ $n=5$	$NiCl_2$ $n=20$	$CuCl_2$ $n=10$
10	—	—	—	—	1,849	—	—
20	0	0	1,639	2,307	3,152	0	1,606
30	—	—	—	—	—	—	2,430
50	—	- 174	2,225	3,242	5,317	1,068	3,308
100	-1,056	- 242	2,355	3,526	6,809	1,380	4,052
200	-1,310	- 258	2,515	3,761	7,632	1,584	4,510
400	-1,410	- 258	—	—	8,020	1,697	—
L_c	-2,360	-7,760	+17,410	+35,920	+15,630	+19,170	+11,080
c	200	200	300	800	300	400	600

A solution of $Na_2I_2+20H_2O$, on dilution up to 40, 100, and 200 formula-weights of water, yields – 914, – 1,740, and – 2,058 thermal units respectively.

HEATS OF HYDRATION AND SOLUTION OF SALTS.

The following table contains the heat of solution of the dehydrated salt, that of the hydrated salt, and the difference between these, which is the heat of hydration. Further, the last column shows the distribution of the heat of hydration among the different formula-weights of water taken up. Thus, with reference to $MnSO_4$, the numbers given in the last column mean that of the total heat of hydration (13,750) 5,990 units are evolved on the addition of the first formula-weight of water, 1,600 on the addition of the second, 1,980 on the addition of each of the third and fourth, and 2,200 on the addition of the last, formula-weight of water which combines with the salt.

The values are valid for a temperature of about 18°C. The heat of hydration increases with the temperature; thus for $MgSO_4 7H_2O$ the increase is 57 units for each increase of 1°C.

Formula of the dehydrated salt	Heat of solution		Number of molecules of water taken up	Heat of hydration	Distribution of the heat of hydration among the different molecules of water
	of the dehydrated salt	of the hydrated salt			
$Na_4P_2O_7$	11,850	− 11,670	10	23,520	10 × 2,352
Na_2HPO_4	5,640	− 22,830	12	28,470	2 × 3,015 + 10 × 2,244
Na_2SO_4	460	− 18,760	10	19,220	1 × 2,360 + 9 × 1,878
Na_2CO_3	5,640	− 16,160	10	21,800	1 × 3,382 + 1 × 2,234 + 6 × 2,109 + 2 × 1,764
K_2CO_3	6,940	− 380	$\frac{3}{2}$	6,870	$\frac{1}{2}$ × 4,420 + 1 × 4,660
$MgSO_4$	20,280	− 3,800	7	24,080	1 × 6,980 + 1 × 2,300 + 2 × 3,400 + 2 × 2,170 + 1 × 3,660
$MnSO_4$	13,790	+ 40	5	13,750	1 × 5,990 + 1 × 1,600 + 2 × 1,980 + 1 × 2,200
$ZnSO_4$	18,430	− 4,260	7	22,690	1 × 8,484 + 2 × 2,346 + 1 × 1,745 + 2 × 2,178 + 1 × 3,417
$CuSO_4$	15,800	− 2,750	5	18,550	1 × 6,460 + 2 × 3,250 + 1 × 2,180 + 1 × 3,410
$CdSO_4$	10,740	+ 2,660	$\frac{8}{3}$	8,080	1 × 4,690 + $\frac{5}{3}$ × 2,034
$K_2Mg(SO_4)_2$	10,600	− 10,020	6	20,620	2 × 4,930 + 2 × 2,950 + 2 × 2,430
$K_2Zn(SO_4)_2$	7,910	− 11,900	6	19,810	2 × 3,731 + 2 × 2,728 + 2 × 3,445
$K_2Cu(SO_4)_2$	9,400	− 13,570	6	22,970	2 × 5,303 + 2 × 2,993 + 2 × 3,186
$K_2Mn(SO_4)_2$	6,380	− 6,430	4	12,810	2 × 4,648 + 2 × 1,760
$NaPtCl_6$	8,540	− 10,630	6	19,170	2 × 4,320 + 2 × 2,540 + 2 × 2,725
$SrCl_2$	11,140	− 7,500	6	18,640	1 × 5,260 + 1 × 3,800 + 2 × 2,460 + 2 × 2,330
$SrBr_2$	16,110	− 7,220	6	23,330	1 × 6,150 + 1 × 3,800 + 3 × 3,120 + 1 × 4,120
$BaCl_2$	2,070	− 4,930	2	7,000	1 × 3,170 + 1 × 3,830
$CaCl_2$	17,410	− 4,340	6	21,750	7,440(2) + 14,310(4)
$MgCl_2$	35,920	+ 2,950	6	32,970	20,940(3) + 2 × 4,370 + 1 × 3,290

HEATS OF SOLUTION OF ALL THE BODIES INVESTIGATED BY THOMSEN.

The materials fall into four groups; the first three of these relate to non-metals, and contain respectively, the heats of solution of gaseous bodies, the heats of solution of liquid bodies, and the heats of solution of solid compounds; the fourth contains the heats of solution of the oxides, hydroxides or hydrated oxides, and salts, of metals.

The tables shew, first, the formula of the compound, and next the quantity of water in the liquid that results from the solution. The quantity of water used for dissolving a hydrated salt is accordingly smaller, by the amount of water in the salt, than the quantity given in the table. When e.g. the table gives the heat of solution of $Na_2SO_4 . 10H_2O$ in 400 formula-weights of water as equal to $-18,760$, this value represents the heat of solution of one formula-weight of the salt, which contains 10 formula-weights of water, in 390 formula-weights of water. For hydrated salts the composition of which was checked analytically the number of formula-weights of water found is given in a special column.

With the exception of the chlorine compounds of silicon, titanium, antimony, bismuth, and tellurium, all the bodies contained in the tables dissolve completely in water. The decomposition by water of the chlorides of the five elements just mentioned is partial.

Compounds of Non-Metals.

a. Gaseous bodies.

Substance (gaseous)	Formula	Formula-weights of water in the solution	Heat of solution for one formula-weight of the body
Hydrochloric acid	HCl	300	17,315
Hydrobromic acid	HBr	400	19,940
Hydriodic acid	HI	500	19,210
Water vapour at 18°	H_2O	—	10,430
Sulphydric acid	H_2S	900	4,560
Ammonia	H_3N	200	8,430
Hypochlorous anhydride	Cl_2O	800	9,440
Nitrogen tetroxide	NO_2	300	7,755
Sulphur dioxide	SO_2	250	7,700
Carbon dioxide	CO_2	1,500	5,880
Carbon oxychloride	$COCl_2$	—	57,970
Carbon oxysulphide	COS	—	6,750

b. Liquid bodies.

Substance (liquid)	Formula	Formula-weights of water in the solution	Heat of solution for one formula-weight of the body
Bromine	Br_2	600	1,080
Sulphur dioxide (liquefied)	SO_2	300	1,500
Sulphur trioxide	SO_3	1,600	39,170
Pyrosulphuric acid	$S_2O_7H_2$	1,600	54,320
Sulphuric acid	SO_4H_2	1,600	17,850
Sulphuric acid hydrate	$SO_4H_2.H_2O$	1,600	11,470
Sulphuryl chloride	SO_2Cl_2	800	62,900
Nitric acid	NO_3H	300	7,480
Phosphoric acid	PO_4H_3	120	5,210
Phosphorous acid	PO_3H_3	120	2,940
Hypophosphorous acid	PO_2H_3	200	2,140
Phosphorus trichloride	PCl_3	1,000	65,140
Phosphorus oxychloride	$POCl_3$	1,100	72,190
Arsenic trichloride	$AsCl_3$	900	17,580
Antimony pentachloride	$SbCl_5$	1,100	35,200
Silicon tetrachloride	$SiCl_4$	3,000	69,260
Titanic chloride	$TiCl_4$	1,600	57,870
Stannic chloride	$SnCl_4$	300	29,920
Formic acid	CH_2O_2	200	150
Acetic acid	$C_2H_4O_2$	200	375

c. Solid compounds of non-metals.

Substance (solid)	Formula	Formula-weights of water in the solution	Heat of solution for one formula-weight of the body
Iodine pentoxide	I_2O_5	—	− 1,790
Iodic acid	IO_3H	200	− 2,170
Periodic acid	IO_6H_5	550	− 1,380
Phosphoric acid	PO_4H_3	120	+ 2,690
Phosphorous acid	PO_3H_3	120	− 130
Hypophosphorous acid	PO_2H_3	200	− 170
Phosphoric anhydride	P_2O_5	550	+ 35,600
Arsenic pentoxide	As_2O_5	—	+ 6,000
Arsenic acid	AsO_4H_3	230	− 400
Arsenious oxide	As_2O_3	—	− 7,550
Selenion dioxide	SeO_2	200	− 920
Oxalic acid	$C_2O_4H_2$	300	− 2,260

Oxalic acid (cryst.)	$C_2O_4H_2.2H_2O$	530	− 8,590
Boric acid (cryst.)	$B_2O_3.3H_2O$	800	− 10,790
Phosphorus pentachloride	PCl_5	1,800	+ 123,440
Antimony trichloride	$SbCl_3$	—	+ 8,910
Bismuth trichloride	$BiCl_3$	—	+ 7,830
Selenion tetrachloride	$SeCl_4$	1,600	+ 30,370
Tellurium tetrachloride	$TeCl_4$	1,200	+ 20,340
Ammonium chloride	NH_4Cl	200	− 3,880
„ bromide	NH_4Br	200	− 4,380
„ iodide	NH_4I	200	− 3,550
„ nitrate	$NH_4.NO_3$	200	− 6,320
„ sulphate	$(NH_4)_2SO_4$	400	− 2,370
„ bisulphate	$NH_4.SO_4H$	200	− 20
Hydroxylamine chloride	$NH_3O.HCl$	200	− 3,650
„ sulphate	$(NH_3O)_2H_2SO_4$	660	− 960
Sulphur triethiodide	$S(C_2H_5)_3I$	267	− 5,750
Tartaric acid	$C_4H_6O_6$	400	− 3,600
Citric acid	$C_6H_8O_7$	600	− 4,100
	$C_6H_8O_7.H_2O$	400	− 6,430
Aconitic acid	$C_6H_6O_6$	300	− 4,180

Oxides, hydroxides, and salts, of the metals.

Metals	Formula	Formula-weights of water in the solution	Heat of solution at about 18° C.	Formula-weights of water according to analysis
Potassium	KCl	200	− 4,440	
	KBr	200	− 5,080	
	KI	200	− 5,110	
	KCN	175	− 3,010	
	KOH	250	+ 13,290	
	KNO_3	200	− 8,520	
	$KClO_3$	400	− 10,040	
	$KBrO_3$	200	− 9,760	
	KIO_3	500	− 6,780	
	K_2CO_3	400	+ 6,490	
	$K_2CO_3.\frac{1}{2}H_2O$	400	+ 4,280	0·507
	$K_2CO_3.\frac{3}{2}H_2O$	400	− 380	1·550
	K_2SO_4	400	− 6,380	
	$KHSO_4$	200	− 3,800	
	$K_2S_2O_6$	500	− 13,010	
	$K_2S_3O_6$	500	− 12,460	
	$K_2S_4O_6$	500	− 13,150	
	$K_2Cr_2O_7$	400	− 16,700	
	$K_2Mn_2O_8$	1,000	− 20,780	
	$K_2C_2O_4.H_2O$	800	− 7,410	
	$KC_2H_3O_2$	200	+ 3,340	

Sodium	$NaCl$	100	− 1,180	
	$NaBr$	200	− 190	
	$NaBr.2H_2O$	300	− 4,710	
	NaI	200	+ 1,220	
	$NaI.2H_2O$	300	− 4,010	
	$NaOH$	200	+ 9,940	
	$NaNO_3$	200	− 5,030	
	Na_2CO_3	400	+ 5,640	
	$Na_2CO_3.H_2O$	400	+ 2,250	
	$Na_2CO_3.2H_2O$	400	+ 20	
	$Na_2CO_3.10H_2O$	400	− 16,160	
	Na_2SO_4	400	+ 460	
		400	+ 170	Melted after exposure to the atmosphere
	$Na_2SO_4.H_2O$	400	− 1,900	
	$Na_2SO_4.10H_2O$	400	− 18,760	10·00
	$NaHSO_4$	200	+ 1,190	
	$Na_2S_2O_6$	400	− 5,370	0·09
	$Na_2S_2O_6.2H_2O$	400	− 11,650	2·13
	$Na_2S_2O_6.5H_2O$	400	− 11,370	
	Na_2HPO_4	400	+ 5,640	
	$Na_2HPO_4.2H_2O$	400	− 390	
	$Na_2HPO_4.12H_2O$	400	− 22,830	12·09
	$Na_2NH_4PO_4.4H_2O$	800	− 10,750	
	$Na_4P_2O_7$	800	+ 11,850	
	$Na_4P_2O_7.10H_2O$	800	− 11,670	10·27
	$Na_2B_2O_7.10H_2O$	1,600	− 25,860	
	$NaC_2H_3O_2.3H_2O$	400	− 4,810	
	$NaC_2H_3O_2$	200	+ 3,870	
Lithium	$LiCl$	230	+ 8,440	
	$LiNO_3$	100	+ 300	
	Li_2SO_4	200	+ 6,050	
	$Li_2SO_4.H_2O$	400	+ 3,410	1·10
Barium	$BaCl_2$	400	+ 2,070	
	$BaCl_2.2H_2O$	400	− 4,930	
	$BaBr_2$	400	+ 4,980	
	$BaBr_2.2H_2O$	400	− 4,130	2·00
	$BaI_2.7H_2O$	500	− 6,850	7·17
	BaO	—	+ 34,520	
	BaO_2H_2	—	+ 12,260	
	$BaO_2H_2.8H_2O$	400	− 15,210	7·98
	BaN_2O_6	400	− 9,400	
	$BaCl_2O_6.H_2O$	600	− 11,240	
	$BaS_2O_6.2H_2O$	400	− 6,930	2·00
	$BaSO_4$	—	− 5,580	
	$Ba(PO_2H_2)_2.H_2O$	800	+ 290	
	$Ba(C_2H_5.SO_4)_2.2H_2O$	800	− 4,970	
	$Ba(C_2H_3O_2)_2.3H_2O$	800	− 1,150	

Strontium	$SrCl_2$	400	+ 11,140	
	$SrCl_2.6H_2O$	400	– 7,500	6·00
	$SrBr_2$	400	+ 16,110	
	$SrBr_2.6H_2O$	400	– 7,220	6·18
	SrO	—	+ 29,340	
	SrO_2H_2	—	+ 11,640	
	$SrO_2H_2.8H_2O$	—	– 14,640	7·95
	SrN_2O_6	400	– 4,620	
	$SrN_2O_6.4H_2O$	400	– 12,300	4·02
	$SrS_2O_6.4H_2O$	400	– 9,250	4·16
Calcium	$CaCl_2$	300	+ 17,410	
	$CaCl_2.6H_2O$	400	– 4,340	6·07
	$CaBr_2$	400	+ 24,510	
	$CaBr_2.6H_2O$	400	– 10,190	6·07
	CaI_2	400	+ 27,690	
	CaO	2,500	+ 18,330	
	CaO_2H_2	2,500	+ 2,790	
	CaN_2O_6	400	+ 3,950	
	$CaN_2O_6.4H_2O$	400	– 7,250	4·20
	$CaS_2O_6.4H_2O$	400	– 7,970	4·14
	$CaSO_4$	—	+ 4,440	
	$CaSO_4.2H_2O$	—	– 300	
Magnesium	$MgCl_2$	800	+ 35,920	
	$MgCl_2.6H_2O$	400	+ 2,950	6·11
	MgO_2H_2	—	0	
	$MgN_2O_6.6H_2O$	400	– 4,220	6·06
	$MgS_2O_6.6H_2O$	400	– 2,960	6·22
	$MgSO_4$	400	+ 20,280	
	$MgSO_4.H_2O$	400	+ 13,300	
	$MgSO_4.7H_2O$	400	– 3,800	
	$K_2Mg(SO_4)_2.6H_2O$	600	– 10,020	6·20
	$K_2Mg(SO_4)_2$	600	+ 10,600	
Beryllium	$BeSO_4.6H_2O$	600	+ 1,550	6·00
Aluminium	Al_2Cl_6	2,500	+ 153,690	
	$K_2Al_2(SO_4)_4.24H_2O$	2,400	– 20,240	
Cerium	$Ce_2(SO_4)_3.4{\cdot}4H_2O$	1,200	+ 16,130	4·38
Yttrium	$Y_2(SO_4)_3.8H_2O$	1,200	+ 10,680	8·04
Didymium	$Di_2(SO_4)_3.8H_2O$	1,200	+ 6,320	8·82
Lanthanum	$La_2(SO_4)_3.8H_2O$	—	+ 4,000?	8·9
Erbium	$Er_2(C_2H_3O_2)_6.8H_2O$	3,000	+ 1,360	
Chromium	$K_2Cr_2(SO_4)_4.24H_2O$	1,600	– 22,300	
	$K_2Cr_2O_7$	400	– 16,700	

ıc	$ZnCl_2$	300	+ 15,630	
	$ZnBr_2$	400	+ 15,030	
	ZnI_2	400	+ 11,310	
	$ZnN_2O_6 . 6H_2O$	400	− 5,840	5·94
	$ZnS_2O_6 . 6H_2O$	400	− 2,420	6·08
	$ZnSO_4$	400	+ 18,430	
	$ZnSO_4 . H_2O$	400	+ 9,950	
	$ZnSO_4 . 7H_2O$	400	− 4,260	7·00
	$K_2Zn(SO_4)_2$	600	+ 7,910	
	$K_2Zn(SO_4)_2 . 6H_2O$	600	− 11,900	6·05
dmium	$CdCl_2$	400	+ 3,010	
	$CdCl_2 . 2H_2O$	400	+ 760	2·10
	$CdBr_2$	400	+ 440	
	$CdBr_2 . 4H_2O$	600	− 7,290	4·06
	CdI_2	400	− 960	
	$CdSO_4$	400	+ 10,740	
	$CdSO_4 . H_2O$	400	+ 6,050	
	$CdSO_4 . \frac{5}{2}H_2O$	400	+ 2,660	2·66
	$CdN_2O_6 . H_2O$	400	+ 4,180	1·00
	$CdN_2O_6 . 4H_2O$	400	− 5,040	4·19
anganese	$MnCl_2$	350	+ 16,010	
	$MnCl_2 . 4H_2O$	400	+ 15,040	3·88
	$MnSO_4$	400	+ 13,790	
	$MnSO_4 . H_2O$	400	+ 7,820	
	$MnSO_4 . 5H_2O$	400	+ 40	5·02
	$MnS_2O_6 . 6H_2O$	400	− 1,930	6·04
	$MnN_2O_6 . 6H_2O$	400	− 6,150	
	$K_2Mn_2O_8$	1,000	− 20,790	
	$K_2Mn(SO_4)_2$	600	+ 6,380	
	$K_2Mn(SO_4)_2 . 4H_2O$	600	− 6,435	4·15
on	$FeCl_2$	350	+ 17,900	
	$FeCl_2 . 4H_2O$	400	+ 2,750	
	Fe_2Cl_6	2,000	+ 63,360	
	$FeSO_4 . 7H_2O$	400	− 4,510	
ɔbalt	$CoCl_2$	400	+ 18,340	
	$CoCl_2 . 6H_2O$	400	− 2,850	5·80
	$CoSO_4 . 7H_2O$	800	− 3,570	7·10
	$CoN_2O_6 . 6H_2O$	400	− 4,960	6·08
ickel	$NiCl_2$	400	+ 19,170	
	$NiCl_2 . 6H_2O$	400	− 1,160	6·02
	$NiSO_4 . 7H_2O$	800	− 4,250	7·03
	$NiS_2O_6 . 6H_2O$	400	− 2,420	6·08
	$NiN_2O_6 . 6H_2O$	400	− 7,470	5·93

Copper	$CuCl_2$	600	+ 11,080	
	$CuCl_2 . 2H_2O$	400	+ 4,210	
	$CuBr_2$	400	+ 8,250	
	$CuSO_4$	400	+ 15,800	
	$CuSO_4 . H_2O$	400	+ 9,320	
	$CuSO_4 . 5H_2O$	400	− 2,750	
	$K_2Cu(SO_4)_2$	600	+ 9,400	
	$K_2Cu(SO_4)_2 . 6H_2O$	600	− 13,570	6·17
	$CuS_2O_6 . 5H_2O$	400	− 4,870	5·00
	$CuN_2O_6 . 6H_2O$	400	− 10,710	6·01
Thallium	Tl_2Cl_2	9,000	− 20,200	
	Tl_2O	570	− 3,080	
	$Tl_2O_2H_2$	470	− 6,310	
	Tl_2SO_4	1,600	− 8,280	
	$Tl_2N_2O_6$	600	− 19,940	
Lead	$PbCl_2$	1,800	− 6,800	
	$PbBr_2$	2,500	− 10,040	
	PbN_2O_6	400	− 7,610	
	$PbS_2O_6 . 4H_2O$	400	− 8,540	4·14
	$Pb(C_2H_3O_2)_2 . 3H_2O$	800	− 6,140	
Tin	$SnCl_2$	300	+ 350	
	$SnCl_2 . 2H_2O$	200	− 5,370	
	$SnCl_4K_2 . H_2O$	600	− 13,420	
	$SnCl_4$	300	+ 29,920	
	$SnCl_6K_2$	800	− 3,380	
Mercury	$HgCl_2$	300	− 3,300	
	$HgCl_4K_2 . H_2O$	600	− 16,390	
	$HgBr_4K_2$	660	− 9,750	
	HgI_4K_2	800	− 9,810	
Silver	$Ag_2N_2O_6$	400	− 10,880	
	Ag_2SO_4	1,400	− 4,480	
	$Ag_2S_2O_6 . 2H_2O$	400	− 10,360	2·38
Gold	$AuCl_3$	900	+ 4,450	
	$AuCl_3 . 2H_2O$	600	− 1,690	2·10
	$AuCl_4H . 4H_2O$	400	− 5,830	4·10
	$AuBr_3$	2,000	− 3,760	
	$AuBr_4H . 5H_2O$	1,000	− 11,400	5·28
Palladium	$PdCl_4K_2$	800	− 13,630	
	$PdCl_6K_2$	—	− 15,000?	

Platinum	$PtCl_4K_2$	600	− 12,220	
	$PtCl_4(NH_4)_2$	660	− 8,480	
	$PtCl_6K_2$	—	− 13,760	
	$PtCl_6Na_2$	800	+ 8,540	
	$PtCl_6Na_2.6H_2O$	900	− 10,630	5·98
	$PtBr_4K_2$	800	− 10,630	
	$PtBr_6K_2$	2,000	− 12,260	
	$PtBr_6Na_2$	600	+ 9,990	
	$PtBr_6Na_2.6H_2O$	800	− 8,550	6·05
	$Pt(NH_3)_4Cl_2.H_2O$	400	− 8,760	

II. *Values determined by various observers.*

HEAT OF SOLUTION OF HYDROFLUORIC ACID[1].

Reaction	Thermal value
[HF, $400H^2O$]	4,560
[HF$5H^2O$, $400H^2O$]	2,050
[HF$1{\cdot}67H^2O$, $400H^2O$]	720
[HF$2{\cdot}25H^2O$, $400H^2O$]	450
[HF$6{\cdot}5H^2O$, $400H^2O$]	100

HEATS OF SOLUTION AND HYDRATION OF CYANIDES[2]. (Temp. 6°—9°.)

Reaction	Thermal value	Remarks
[NaCN, $100H^2O$]	− 500	Solution of cyanides and hydrated cyanides.
[NaCN$2H^2O$, $100H^2O$]	− 4,410	
[NaCN$\frac{1}{2}H^2O$, $100H^2O$]	− 1,010	
[$Ba(CN)_2$, $200H^2O$]	1,780	
[$Ba(CN)_2H^2O$, $200H^2O$]	2,100	
[$Ba(CN)_22H^2O$, $200H^2O$]	− 5,760	
[$Hg(CN)_2$, Aq]	− 3,000[3]	
[NaCN, $2H^2O$]	3,910	Formation of hydrates by action of liquid water.
[NaCN, $\frac{1}{2}H^2O$]	510	
[$Ba(CN)_2$, H^2O]	3,880	
[$Ba(CN)_2$, $2H^2O$]	6,140	

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[1] Guntz, *Bull. Soc. Chim.* (2). **40**. 54.

[2] Joannis, *Compt. rend.* **92**. 1338—1341.

[3] Berthelot, *Compt. rend.* **77**. 388.

Heats of solution of sulphides[1]. (Temp. 15°—17°).

Salt	Quantity of water	Heat of solution
Na^2S	130—140 parts	15,000
Na^2S5H^2O	60—120 „	- 6,600
Na^2S9H^2O	60—105 „	- 16,720
Na^2SH^2S	104—830 „	8,800
$Na^2SH^2S4H^2O$	60—100 „	- 3,060
K^2SH^2O	230 „	3,800
K^2S5H^2O	75— 90 „	- 5,200
K^2SH^2S	40—400 „	1,540
$K^2SH^2SH^2O$	45—240 „	1,340
NH^4S^2	150 „	- 4,100
Reaction		
[CaS, Aq]		6,100
[SrS, Aq]		6,800
[BaS, Aq]		7,000

Heats of solution and hydration of chromic acid and chromates[2].

Reaction	Thermal value	Remarks
$[CrO^3, H^2O]$	580	Heat of formation of liquid H_2CrO_4.
$[CrO^4H^2, H^2O]$	340	Addition of definite quantities of water to solutions of $H_2Cr_2O_4$ of specified composition as regards quantities of H_2CrO_4 and H_2O; $Q = H_2CrO_4$.
$[QH^2O, H^2O]$	260	
$[Q2H^2O, H^2O]$	135	
$[Q3H^2O, H^2O]$	171	
$[Q4H^2O, H^2O]$	80	
$[Q5H^2O, H^2O]$	35	
$[Q5H^2O, 25H^2O]$	500	
$[Q30H^2O, 25H^2O]$	210	
$[Na^2CrO^4, 4H^2O]$	9,800	Formation of hydrates by action of liquid water.
$[Na^2CrO^4, 10H^2O]$	18,000	

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[1] Sabatier, *Compt. rend.* **89**. 43: **91**. 52. *Ann. Chim. Phys.* (5). **22**. 98.

[2] Morges, *Compt. rend.* **86**. 1444 Berthelot, *Compt. rend.* **87**. 574.

HEATS OF SOLUTION AND HYDRATION OF PERCHLORIC ACID AND PERCHLORATES[1]. (Temp. 19°—20°).

Reaction	Thermal value	Remarks
$[HClO^4, Aq]$	20,300	Solution of liquid $HClO_4$.
$[HClO^4H^2O, Aq]$	7,700	Solution of crystallised $HClO_4H_2O$.
$[HClO^4H^2O, Aq]$	about 11,700	Solution of liquid $HClO_4H_2O$.
$[HClO^42H^2O, Aq]$	5,300	„ „ $HClO_42H_2O$.
$[KClO^4, Aq]$	$-12,100$	Solution of various solid perchlorates.
$[NaClO^4, Aq]$	$-3,500$	
$[Ba^{\frac{1}{2}}ClO^4, Aq]$	-900	
$[NH^4ClO^4, Aq]$	$-6,300$	
$[HClO^4, H^2O]$	12,600	Formation of solid $HClO_4H_2O$ from liquid $HClO_4$ and liquid H_2O.
$[HClO^4, H^2O]$	7,400	Formation of liquid $HClO_4H_2O$ from liquid $HClO_4$ and liquid H_2O.
$[HClO^4H^2O, H^2O]$	6,400	Formation of liquid $HClO_4 2H_2O$ from liquid constituents.

HEATS OF SOLUTION OF ALUMS[1]. (One formula-weight in about 1000 formula-weights of water).

Salt	Heat of solution	
	at 8°—11°	at 19°—21°
$K^2Al^24SO^424H^2O$	$-19,600$	$-19,760$
$(NH^4)_2Al^24SO^424H^2O$	$-19,160$	$-19,260$
$K^2Cr^24SO^424H^2O$	$-19,300$	$-19,000$
$(NH^4)_2Cr^24SO^424H^2O$	$-19,250$	$-19,780$
$K^2Fe^24SO^424H^2O$	$-32,030$	
$(NH^4)_2Fe^24SO^424H^2O$	$-33,140$	$-36,120$

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[1] Berthelot, *Compt. rend.* **93**. 241.

[2] Favre and Valson, *Compt. rend.* **74**. 1019.

HEATS OF SOLUTION OF SOME DOUBLE SALTS, AND OF THE CONSTITUENTS OF THESE SALTS[1].

Salt	Heat of solution	Sum of (1) and (2) =A	Double salt	Heat of solution =B.	Difference B - A
K^2SO^4	-6,340	-8,770	$K^2SO^4CuSO^46H^2O$	-14,360	- 5,590
$CuSO^45H^2O$	-2,430				
$(NH^4)_2SO^4$	-1,940	-4,370	$(NH^4)_2SO^4CuSO^46H^2O$	-11,240	- 6,870
$CuSO^45H^2O$	-2,430				
K^2Cl^2	-9,150	-4,500	$K^2Cl^2CuCl^2H^2O$	- 6,980	- 2,480
$CuCl^22H^2O$	+4,650				

HEATS OF SOLUTION OF BUTYRATES[2] AND SUCCINATES[3].

Reaction	Thermal value	Remarks
$[C^4H^7NaO^2, Aq]$	4,270	Solution of sodium butyrate dried at 100°.
$[C^4H^7NaO^2, Aq]$	4,210	Solution of sodium butyrate dried in vacuo.
$[C^4H^7NaO^2\frac{1}{2}H^2O, Aq]$	3,660	Solution of hydrated sodium butyrate.
$[C^4H^7NaO^23H^2O, Aq]$	3,440	Solution of hydrated sodium butyrate.
$[C^4H^7NaO^2, \frac{1}{2}H^2O]$	580	Formation of various hydrates of sodium butyrate, by action of liquid water.
$[C^4H^7NaO^2\frac{1}{2}H^2O, \frac{5}{2}H^2O]$	220	
$[C^4H^7NaO^2, 3H^2O]$	800	
$[C^4H^4Na^2O^4, Aq]$	8,400	Solution of sodium and potassium succinates. (Temp. 8° - 11°).
$[C^4H^4Na^2O^46H^2O, Aq]$	-11,000	
$[C^4H^4K^2O^4, Aq]$	200	
$[C^4H^4K^2O^4H^2O, Aq]$	- 3,400	
$[C^4H^4KHO^4H^2O, Aq]$	- 7,600	
$[C^4H^4(NH^4)HO^4, Aq]$	- 4,900	
$[C^4H^4Na^2O^4, 6H^2O]$	19,400	Formation of hydrates of sodium and potassium succinates by action of liquid water.
$[C^4H^4K^2, H^2O]$	3,600	

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[1] Favre and Valson, *loc. cit.* **73**. 1150.

[2] Berthelot, *Compt. rend.* **80**. 512.

[3] Chroustchoff, *Compt. rend.* **89**. 579.

HEATS OF SOLUTION OF AMINES[1].

Reaction	Thermal value	Remarks
$[NH^2(C^2H^5), Aq]$	12,910	Solution of ethylamine in about 400 H_2O at 19°.
$[N(CH^3)_3, Aq]$	12,900	Solution of trimethylamine in about 270 H_2O at 20°.

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[1] Berthelot, *Compt. rend.* **91.** 141.

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